

D E C L A R A T I O N

In the matter of U.S. Patent  
Appln. Ser. No. 09/374,344  
in the name of TOTO LTD.

I, KONNO Akio, of Kyowa Patent and Law Office, 2-3,  
Marunouchi 3-Chome, Chiyoda-Ku, Tokyo-To, Japan, declare  
and say:

that I am thoroughly conversant with both the Japanese  
and English languages; and,

that the attached document represents a true English  
translation of Japanese Patent Application No. 7-354649  
filed on December 22, 1995.

I further declare that all statements made herein of  
my own knowledge are true and that all statements made on  
information and belief are believed to be true; and further  
that these statements were made with the knowledge that  
willful false statements and the like so made are punishable  
by fine or imprisonment, or both, under Section 1001 of Title  
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Dated: July 4, 2003

  
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7-354649

Name of Document: Patent Application

Reference Number: 955771

Application Date: December 22, 1995

To: The Commissioner of the Patent Office

International Patent Classification: A61L9/00

Title of the Invention: METHOD OF RENDERING A MEMBER  
SURFACE HYDROPHILIC, METHOD OF  
IMPROVING, MAINTAINING AND  
RECOVERING HYDROPHILICITY  
THEREOF, AND METHODS OF RENDERING  
A MEMBER RESISTANT TO STAIN,  
ANTIFOGGING AND ANTICONDENSING  
THEREOF

Number of Claim(s): 34

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Indication of Fee:

Deposit Account Number: 017640

Fee: 21,000 (yen)

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SPECIFICATION

1. TITLE OF THE INVENTION

METHOD OF RENDERING A MEMBER SURFACE HYDROPHILIC, METHODS OF IMPROVING, MAINTAINING AND RECOVERING HYDROPHILICITY THEREOF, AND METHODS OF RENDERING A MEMBER RESISTANT TO STAIN, ANTIFOGGING AND ANTICONDENSING THEREOF

1. CLAIMS

1. A method of rendering hydrophilic wherein a layer comprised of physically absorbed water is formed on a member outermost surface.

2. A method of improving hydrophilicity wherein the amount of physically absorbed water formed is increased on a member outermost surface.

3. A method of maintaining hydrophilicity wherein a layer comprised of physically absorbed water formed is maintained on a member outermost surface.

4. A method of recovering hydrophilicity wherein a layer comprised of physically absorbed water is reformed on a member outermost surface.

5. A method of improving the hydrophilicity of a member surface according to claim 2, comprising the steps of:  
forming on a substrate surface a layer containing a



hydrophilic substance and a photo semiconductor, and irradiating a UV on said surface.

6. A method of maintaining the hydrophilicity of a member surface according to claim 3, comprising the step of: irradiating constantly a UV on a member surface wherein a layer containing a hydrophilic substance and a photo semiconductor is formed on a substrate surface.

7. A method of maintaining the hydrophilicity of a member surface according to claim 3, comprising the step of: irradiating constantly a UV at intervals of the desired time or less on a member surface wherein a layer containing a hydrophilic substance and a photo semiconductor is formed on a substrate surface.

8. A method of recovering the hydrophilicity of a member surface according to claim 4, comprising the step of: re-irradiating a UV on a member surface wherein a layer containing a hydrophilic substance and a photo semiconductor is formed on a substrate surface.

9. A method of improving the hydrophilicity of a member surface according to claim 2, comprising the steps of: forming on a substrate surface a layer containing a hydrophilic substance, a photo semiconductor and an accumulated water substance, and irradiating a UV on said surface.

10. A method of maintaining the hydrophilicity of a member

surface according to claim 3, comprising the step of:  
irradiating constantly a UV on a member surface wherein a  
layer containing a hydrophilic substance, a photo  
semiconductor and an accumulated water substance is formed  
on a substrate surface.

11. A method of maintaining the hydrophilicity of a member  
surface according to claim 3, comprising the step of:  
irradiating constantly a UV at intervals of the desired time  
or less on a member surface wherein a layer containing a  
hydrophilic substance, a photo semiconductor and an  
accumulated water substance is formed on a substrate  
surface.

12. A method of recovering the hydrophilicity of a member  
surface according to claim 4, comprising the step of:  
re-irradiating a UV on a member surface wherein a layer  
containing a hydrophilic substance, a photo semiconductor  
and an accumulated water substance is formed on a substrate  
surface.

13. Methods of improving, maintaining and recovering the  
hydrophilicity of a member surface according to claims 5 -  
8, wherein said layer containing a hydrophilic substance and  
a photo semiconductor is a titanium oxide containing layer  
having an outermost surface comprised of inorganic oxide  
hydrophilic on a substrate surface.

14. Methods of improving, maintaining and recovering the  
hydrophilicity of a member surface according to claims 5 -

8, wherein said layer containing a hydrophilic substance and a photo semiconductor is a tin oxide containing layer having an outermost surface comprised of inorganic oxide hydrophilic on a substrate surface.

15. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claims 9 - 12, wherein said layer containing a hydrophilic substance, a photo semiconductor and an accumulated substance on a substrate surface is a layer containing titanium oxide and a silicon oxide compound having an outermost surface comprised of inorganic oxide hydrophilic on a substrate surface.

16. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claim 15, wherein said silicon oxide compound is silicon dioxide or a silanol resin.

17. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claim 15, wherein said silicon oxide compound is silicon dioxide, and the mol fraction of the silicon dioxide versus the sum of the titanium oxide and silicon dioxide is 5 - 25%.

18. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claim 13, wherein one kind or more metals and/or ion thereof selected from Ca, K, Na, Mg, Li, Zn, Sr, Pt, Pd, Ni, Fe, Ag, Cu and Ru are contained in said titanium oxide containing layer.

19. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claim 13, wherein one kind or more metals and/or ion thereof selected from Ca, K, Na, Mg, Li, Zn, Sr, Pt and Pd are further contained in said titanium oxide containing layer.

20. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claim 13, wherein one kind or more substances selected from aluminum oxide, zirconium oxide, cerium oxide and tin oxide are further contained in said titanium oxide containing layer.

21. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claim 13, wherein tin oxide is further contained in said titanium oxide containing layer.

22. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claim 21, wherein the ratio by weight of the tin oxide versus the sum of the titanium oxide and tin oxide is 1% or more and less than 95%.

23. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claim 21, wherein the ratio by weight of the tin oxide versus the sum of the titanium oxide and tin oxide is 1% or more and 50% or less.

24. Methods of improving, maintaining and recovering the

hydrophilicity of a member surface according to claim 14, wherein Ag is further contained in said tin oxide containing layer.

25. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claim 13, wherein the average crystal diameter of the titanium oxide in said titanium oxide containing layer is less than 800 nm.

26. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claim 13, wherein the average crystal diameter of the titanium oxide in said titanium oxide containing layer is 300 nm or less.

27. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claim 13, wherein said titanium oxide containing layer is comprised by the steps of: applying organic titanium on a substrate, hydrolyzing the organic titanium to obtain amorphous titanium oxide, and crystallizing the amorphous titanium oxide.

28. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claim 13, wherein said titanium oxide containing layer is comprised by the steps of: applying on a substrate a titanium oxide sol, and heat-calcining thereof.

29. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claim 13,

wherein said titanium oxide containing layer is comprised by the steps of: applying on a substrate metal titanium, and oxidizing the metal titanium for crystallization.

30. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claims 5 - 8, wherein said layer containing a hydrophilic substance and a photo semiconductor is comprised by the steps of: applying on a substrate a photo semiconductor sol and a hydrophobic resin having a main chain with photo resistance and a side chain hydrophobic to be decomposed with a UV, curing the hydrophobic resin, and substituting by the photo semiconductor action at least the side chain hydrophobic in said hydrophobic resin on the substrate surface with a hydroxyl group.

31. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claims 15, wherein said layer containing titanium oxide and a silicon oxide compound is comprised by the steps of: applying on a substrate titanium oxide and a siloxane resin containing an organic group chemically-bonded with a silicon atom, curing said siloxane resin, and oxidatively-decomposing by the titanium oxide photocatalytic action said organic group to be substituted with a hydroxyl group.

32. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claims 5 - 31, wherein said light source irradiating a UV is a sunray.

33. Methods of improving, maintaining and recovering the hydrophilicity of a member surface according to claims 5 - 31, wherein said light source irradiating a UV is general indoor illumination.

34. Methods of rendering a member resistant to stain, antifogging and anticondensing thereof, wherein a method of rendering hydrophilic and methods of improving, maintaining and recovering the hydrophilicity according to claims 1 - 33 are used.

[Detailed Description of the Invention]

[0001]

[Technical Field]

The present invention relates to a method of rendering a member surface hydrophilic or a method of improving thereof, so as to provide the member surface with characteristics of stain resistance, self-cleaning, cleaning facility, antifogging and anticondensing. More particularly, it relates to methods of maintaining the hydrophilicity for a long period and of recovering thereof as necessary.

[0002]

[Prior Art]

Conventionally, to render an exterior building material resistant to stain, a method of forming a water-repellent resin film on a member surface has been suggested. However, recently it has been apparent that, in a method of forming a water-repellent resin film like polytetrafluoroethylene on a member surface, hydrophobic stains are retained on a member

after water is dried thereon, being noticeable  
("Highpolymer", vol. 44, page 307 (1995)).

For example, a black, vertical pattern of stain produced on the external wall of a structural building is comprised of a hydrophobic substance like carbon black, a burned product (Scientific Lecture Summary of Japan Architecture Meeting, Oct. 1987), and is flown with flowing-down water onto the a material surface to be generated (Construction Reports of Japan Architecture Meeting, No. 404, Oct. 1989).

Therefore, when a material surface is painted with a general hydrophobic paint or a water-repellent paint, the above hydrophobic stain easily conforms to the material surface compared with water, so that the stain is hard to be washed off by rain, resulting in retention on the material surface, or being moved slightly to form a vertical pattern of stain.

[0003]

Based on the above facts, a method of applying a hydrophilic paint on an external wall has been suggested in order to avoid a black, vertical pattern of stain produced on the external wall of a structural building ("Highpolymer", vol. 44, page 307 (1995)).

Further, there has been a building material comprised of inorganic glass with a smooth surface like a glazed tile, as a stain-resistant building material. It is known that an inorganic glass material like a glazed tile is a hydrophilic material.

[0004]

Also, conventionally, a neutral detergent has been used



in order to wash off oil stains on a kitchen sink tank and tableware, hand dirt adhered to a windowpane. For that reason, there are problems shown below.

(1) Discharging drain causes an environmental problem like water quality pollution.

(2) A neutral detergent may cause skin damage.

[0005]

To solve these problems, there is, e.g. a method of coating on a glass surface the 10 nm thickness water-soluble salts such as sodium tripolyphosphoric acid and sodium tetraborate to wash thereof off with water (Newspaper "Daily Chemical Industry", Oct. 7, 1994).

[0006]

Also, conventionally a method of rendering resistant to stain, using a photocatalyst to oxidatively decompose an organic substance has been suggested. For example, Japanese Patent Publication No. 51646/1995 disclosed "A method of cleaning stain on a solid surface comprising the steps of holding a photo semiconductor particle on a solid surface that may cause stain due to adhesion of an organic substance in the air, then irradiating a UV light on the photo semiconductor particle, and decomposing the organic substance adhered to the solid surface."

[0007]

Also, conventionally there has been a big problem that fogging is produced on a vehicle window and mirror, showcase with a refrigerator, bathroom mirror, reflective mirror, window of a high-rise building or viewing bathroom.

In other words, the fogging problems are as follows: fogging on a vehicle window and mirror, and reflective

mirror will cause difficulty in safe driving in rain; fogging on a showcase with a refrigerator will allow goods to be unseen by consumers; fogging on a bathroom mirror will not deliver an original function as a full-length mirror; and fogging on the window of a high-rise building or viewing bathroom will not allow a beautiful scene to be seen.

[0008]

The following mechanism will cause fogging on a member surface. First, a steam molecule above saturated vapor pressure is produced by a change in temperature and an increase in humidity on a member surface. Then, the steam molecule for supersaturated content is liquefied, and adheres to the member surface to grow into a droplet. When the size of the droplet is about  $1/2$  of the wavelength of a visible light, the light is scattered remarkably to be visually felt as fogging.

[0009]

Conventionally, to render the above member antifogging, a method of preventing saturated vapor pressure from being reached in an atmosphere around the member, has mainly been adopted.

For example, to prevent antifogging of a showcase with a refrigerator, the inside of the showcase is refrigerated to store goods, and at the same time, an electric heating element is provided on the inner wall surface of the showcase.

Also, a vehicle window, e.g. of a bullet train, is made double so that the temperature of the inside of the window is not lower than room temperature by outside cold air.

Laminated glass is used for an automobile windshield,

and a heat insulator is inserted therein. Further, dry air (warm wind) is sprayed on the inside of an automobile windshield.

[0010]

Furthermore, in recent years, to prevent antifogging on a member, it has been suggested that a film comprised of a hydrophilic resin is stuck on a member surface.

For example, Japanese Utility Model Loid-open Publication No. 136489/1992 disclosed "An antifogging refrigerating apparatus wherein a refrigerating room partitioned with a heat insulator casing and a glass plate and a freezing cycle evaporator in the refrigerating room are provided, or air cooled with the freezing cycle evaporator is blown, said refrigerating apparatus comprising: sticking a transparent antifogging film on the refrigerator room side of a transparent plate like a glass plate forming said refrigerator room." In addition, the preferable embodiment suggests that "said antifogging film contains a polymer and a hydrophilic monomer on a supporting film surface and forms a hydrophilic film cross-linked by irradiating an electron radiation." The hydrophilic film used here is made by cross-linking a polyacrylic acid alkyl ester polymer with a hydroxyl group, carboxyl group, amide group and imide group.

[0011]

Furthermore, condensation is a problem in an antenna, solar battery, high-voltage power transmission line, heat exchanger, plastic greenhouse ceiling and snow country roof material.

For example, in winter, snow accumulated on the surface

of an antenna melts a little to become a droplet.

This droplet as an adhesive allow snow accumulation to be promoted rapidly, causing communication interference. The droplet formed on a solar cell, serves as a convex lens, heat-damaging the cell.

The droplet adhered to a high-voltage power transmission line becomes conical in shape for arc discharge, leading to power loss and electric wave failure.

The droplet adhered between the fins of the heat exchanger of an air conditioner placed outside a room to be frozen, will allow the efficiency of the machine to be lowered.

The droplet adheres easily to a particular position of the inside of a plastic greenhouse ceiling, dropping on a planted crop thereunder to rot the root.

It is thought that the droplet on a snow country roof material becomes an ice nucleus to accumulate much snow thereon.

For that reason, the load of the snow on the roof is high, requiring frequent maintenance of the roof.

[0012]

At present, to solve the problems of an antenna, high-voltage power transmission line and heat exchanger, it has been suggested that a thin film of aluminum fluoride is coated thereon (Newspaper "Nihon Keizai Shimbun" Aug. 17, 1994).

[0013]

[Problems to be Solved by the Invention]

Hydrophilic paints used conventionally are: an acrylic silicon resin, aqueous silicon coating agent, graft polymer

of silicon and acrylic resins (Japanese Utility Model Loid-open Publication No. 68006/1993), block polymer of silicon and acrylic resins, acrylic resin, acrylic-styrene resin, sorbic fatty acid ethylene oxide, urethane acetate, sorbic fatty ester (Japanese Utility Model Loid-open Publication No. 72004/1993), cross-link form urethane comprised of polycarbonate diol and/or polyisocyanate, and polyacrylic acid alkyl ester cross-link. The contact angle with water is of the order, at most, of 70°; the angle is of the order, at most, of 50°, although the paint coated on an exterior building material allows the hydrophilicity to be improved a little by rain within several months. For that reason, as shown in Japanese Patent Application No. 99425/1995, it is hard to prove that a sufficient effects work in stain resistance. Also, in the case where such paint is coated on an exterior building material, initially the angle of 70° or more with hydrophobicity causes stains so often; and it takes several months for hydrophilization to 50°. After all, a stain resistant effect by weak hydrophilicity can be obtained after that.

[0014]

Also, a building material comprised of inorganic glass with a smooth surface like a glazed tile, shows a favorable result of a contact angle with water of about 5 - 20° at production; but as time passes, a component such as lower carboxylic acid and surfactant, including both of a hydrophilic functional group and a hydrophobic functional group, adheres to the material surface to render thereof hydrophobic ("Design of Glass Surface" Kindai Henshu-sha, (1983)). Therefore, low hydrophilicity cannot be maintained

for a long period to be deteriorated to about 30 - 50'. For that reason, the material can be expected to have a stain-resistant effect slightly better than that of the above paints, but it is hard to say it works a sufficient effect. In the same way, since a thin film of aluminum fluoride has no maintaining function, hydrophilicity maintenance cannot be expected for a long period.

[0015]

Also, conventional antifogging has the following disadvantages.

- (1) In refrigerating the inside of a showcase to store goods, and providing an electric heating element on the inner wall of the showcase, cooling and heating are performed in the same space, and a heater must be ON constantly for keeping its effect. Therefore, running cost is excessive and uneconomical.
- (2) In making a window double so that the temperature of the inside of the window is not lower than room temperature by outside cold air, two windows must be provided. Therefore, this needs excessive initial cost, much time for cleaning the windows, and additional space to provide one more window. Further, only fogging resulting from a difference in a temperature between the inside and the outside, can be prevented; thus, in the case where the humidity is higher in a room and exceeds the saturated vapor pressure, this method cannot be responded.
- (3) Using laminated glass to insert a heat insulator therein needs excessive initial cost. Also, only fogging resulting from a difference in a temperature between the inside and the outside, can be prevented; thus, in the case where the

humidity is higher in a room and exceeds the saturated vapor pressure, this method cannot be responded.

(4) Spraying dry air (warm wind) on the inside of a glass, dries room air and increases room temperature, limiting used conditions. In other words, dried room air adversely affects a throat, and increased room temperature involves discomfort for use in summer.

(5) Applying a conventional hydrophilic film cannot maintain hydrophilicity for a long period, not keeping an antifogging effect.

[0016]

Also, using a photocatalyst delivers its power under indoor illumination of the order of  $0.001 - 1 \text{ mW/cm}^2$ , in decomposing gas such as methylmercaptan and ammonia, and antibacterial property (to be understood that a sufficient effect is provided at active oxygen concentration exceeding the process ability of enzymic catalase held by bacteria) (No. WO94/11092). In a method of rendering resistant to stain wherein a conventional photocatalyst is used to oxidatively decompose an organic substance, to deliver stain resistance by completely oxidatively decomposing highpolymer organic adherents like oil, the amount of the photocatalyst, film thickness and the amount of UV must be increased to raise the generated amount of active oxygen by the photocatalyst. For example, according to Japanese Patent Publication No. 51646/1995, in the case of cooking oil, it takes 3 hours for a  $7.5 \text{ } \mu\text{m}$  film thickness and a  $7 \text{ mW/cm}^2$  UV (10 times or more the amount of a sunray UV). A thick film with a  $7.5 \text{ } \mu\text{m}$  film thickness, will lose transparentness in a transparent member and make it hard to maintain a

sufficiently high surface hardness. Also, a  $7 \text{ mW/cm}^2$  UV is a light amount far exceeding a sunray and indoor illumination, and cannot be applied to most of uses indoors and outdoors.

[0017]

In view of the above facts, it is an object of the present invention to offer a method of rendering fully a member surface hydrophilic, a method of maintaining hydrophilicity thereof for a long period, and a method of recovering the hydrophilicity of a member surface that lost thereof by being kept in the dark once, and thereby to provide a member that can, for a long period, deliver completely its sufficient stain resistance in a sunray and indoor illumination, antifogging, anticondensing, self-cleaning by rainfall, and cleaning facility only by washing with water.

[0018]

Means to Solve the Problems and Effects To solve the above problems, the present invention offers methods of improving, maintaining and recovering the hydrophilicity of a member surface comprised of the steps of: forming on a substrate surface a layer containing a hydrophilic substance like metal oxide and a photo semiconductor like titanium oxide, and irradiating thereon a UV.

The inventor of the present invention found for the first time in the world that, a layer containing a hydrophilic substance and a photo semiconductor is formed on a substrate surface so that the amount of physically absorbed water on the member surface is increased by irradiating a UV to improve the hydrophilicity; the



physically absorbed water layer is present on the member surface as long as subjected to a UV so that the hydrophilicity is maintained; or a physically absorbed water layer is formed on a member surface by irradiating a UV so that the hydrophilicity is recovered (a series of these effects is hereinafter called "Photo hydrophilic effect"). This can improve, maintain and recover stain resistance, antifogging and anticondensing.

[0019]

This construction is common to a photocatalyst action in inclusion of the steps of forming a layer containing a photo semiconductor like titanium oxide and irradiating thereon a UV. However, their operating principles and basic constructions for strengthening functions, are essentially different.

[0020]

In the photocatalyst action, a photo semiconductor like titanium oxide plays a photocatalyst role that generates a hole and an electron from a photon to produce active oxygen such as radical hydroxide with reaction of the hole and ion hydroxide, and superoxide ion with reaction of the electron and an oxygen molecule. In other words, light, oxygen and water are made to react through a titanium oxide surface (photocatalytically active point) to produce active oxygen. Therefore, the following characteristics occurs in the photocatalytic action.

(1) Adhesion of an inactivated substance to a photocatalytically active point, will make it hard to produce photocatalytic activation.

For example, when titanium oxide is used as white

pigment, in order not to deteriorate (decompose) a body material resin by the photocatalytic action, alumina, silica, zirconia, antimony oxide, amorphous titanium oxide, water-containing titanium oxide, zinc, aluminum, magnesium, antimony and manganese, are added ("Titanium Oxide", Gihodo (1991)). A photocatalytically active point is covered by the above substances, losing most of photocatalytic activation.

Also, in a water environment, the photocatalytically active point only with titanium oxide is covered by a metal ion in the water such as calcium and magnesium, reducing the photocatalytic activation during long use. To prevent this, application for antibacterial sanitary ware and tiles can be used by covering the photocatalytically active point beforehand with a metal having electron uptake properties such as copper and silver, and strengthening the photocatalytic activation (Japanese Patent Publication No. 232080/1995).

Therefore, the active point is covered with calcium and magnesium ions, losing the photocatalytic activation. In the case of extremely great dust deposit and highpolymer concentration for a long period, these cover the active point, making it hard to deliver the photocatalytic activation. For that reason, the member surface can be used by being subjected to a  $2 \text{ mW/cm}^2$  or more UV with a 250 nm wavelength (Japanese Patent Publication No. 7905/1994), by heat-regenerating at high temperatures (Japanese Patent Publication No. 7906/1994), and by covering the above photocatalytically active point beforehand with a metal having electron uptake properties such as copper and silver,

and strengthening the photocatalytic activation.

(2) In reaction requiring, in particular, high activated energy for oxidatively decomposition, e.g. in decomposing highpolymer and oil, the density of a photon or photocatalytic activation, is increased to gain the reactive speed remarkably.

To increase the density of the photon, a UV intensity is raised.

To enhance the photocatalytic activation, a photocatalytic surface area that can contact a photon must be increased; concretely, there are methods of: enhancing a UV wavelength to have energy exceeding the forbidden band width of a photo semiconductor to increase a UV attained depth; and increasing a photocatalytic surface area itself due to the increased amount of the photocatalyst in a film component, an increased film thickness of a photocatalyst, and a particulated photocatalytic particle.

In other words, the above photocatalytic action has extremely high dependence on the above UV intensity, UV wavelength, the amount of the photocatalyst in a film component, a film thickness of a photocatalyst and a photocatalyst particle diameter.

[0021]

On the contrary, as apparent from the embodiments described later, the photo hydrophilic effect of a photo semiconductor like titanium oxide of the present invention, is clearly different from a conventional photocatalytic effect:

(1) The photo hydrophilic effect can be delivered in the same way, even if alumina, silica, zirconia, antimony oxide,

amorphous titanium oxide, zinc, aluminum, magnesium and calcium, are added. Reversely, it proves that silica has an effect of improving the photo hydrophilic effect remarkably.

(2) Stain resistance of adhered highpolymer and oil are not proved to have dependence on a UV wavelength, the amount of the photocatalyst in a film component, and a photocatalyst film thickness.

[0022]

Also, the photo hydrophilic effect of the photo semiconductor like titanium oxide of the present invention, has a mechanism different from that of a member like a general glazed tile comprised only of the outermost surface of a conventional hydrophilic substance.

In other words, in a surface construction comprised of an inorganic hydrophilic substance like a general glazed tile, a stain component with an amphoteric functional group such as carboxylic acid, alcohol and surfactant other than water, is comparably easy to adhere to an surface asymmetric group. Therefore, although the construction has the hydrophilicity at production, it is gradually rendered hydrophobic because of no maintaining mechanism.

[0023]

On the contrary, in the present invention, the photo semiconductor action of titanium oxide subjected to a UV, generates a hole and an electron, and thereby the polarity of a substrate surface hydrophilic is raised to increase the amount of the physically absorbed water on the substrate surface, improving the hydrophilicity As long as a physically absorbed water layer is maintained on the substrate surface, stains hydrophobic and having an

amphoteric functional group cannot adheres to the substrate, maintaining the hydrophilicity as well as stain resistance.

Further, the substrate is kept in an environment without subjected to a UV so that even if stains hydrophobic and having an amphoteric functional group adheres to the substrate, the amount of the physically absorbed water on the substrate surface is formed and increased simply by being subjected to a UV, thus these stains cannot adhere to the substrate, recovering the hydrophilicity as well as stain resistance.

[0024]

Furthermore, the hydrophilicity is improved, maintained and recovered so that no droplet is formed on a member surface to prevent condensation and do not scatter a visible light for antifogging.

[0025]

The further preferable embodiment of the present invention includes the steps of: forming on a substrate surface a layer containing a hydrophilic substance, a photo semiconductor and an accumulated water substance, and irradiating thereon a UV.

The accumulated water substance like silica other than the hydrophilic substance and photo semiconductor, is contained in a substrate surface, so that in addition to an increase in the physically absorbed water and the maintaining effect by the photo semiconductor, the accumulated water substance like silica accumulates water in the construction to discharge thereof gradually, thus improving the hydrophilicity by being subjected to a weaker UV. Also, a hydrophobic phenomenon kept in the dark can be

delayed to maintain the hydrophilicity with UV irradiation for a longer period.

[0026]

[Embodiment of the Invention]

The concrete construction of the present invention is explained below. The basic construction of the present invention is comprised of methods of improving, maintaining and recovering the hydrophilicity of a member surface including the steps of: forming on a substrate surface a layer containing a hydrophilic substance like a metal oxide and a photo semiconductor like titanium oxide, and irradiating thereon a UV.

The hydrophilicity refers to a tendency conforming to water, and for a solid material, to a low contact angle with water. In general, it is pointed that a hydrophilic resin has a contact angle with water of less than 90°, and this definition should be followed here (However, conveniently the embodiments later describe that "hydrophilicity" has a low contact angle with water (about 30° or less) to a degree that the angle exceeds the technical standard of a conventional hydrophilic resin.

The hydrophilic substance is a solid with a contact angle with water of less than 90°, as its original characteristic of the contact angle with water, i.e. in a condition without contamination on a surface.

Such substances include: a metal oxide such as titanium oxide, silica, tin oxide, zinc oxide, iron oxide, tungsten oxide, zirconium oxide, yttrium oxide, aluminum oxide, copper oxide, antimony oxide and cerium oxide; an inorganic oxide of a complex oxide such as strontium titanate and

barium titanate; and a silicon resin containing in a side chain a large amount of polar functional groups like a hydroxyl group.

The photo semiconductor refers to a semiconductor wherein the electron of a valence electron band is hard to be excited on a conductive band, with the energy amount of the order of phonon oscillation, but not with a photon below a particular wavelength subjected to a UV, to generate a conductive electron and a hole. Concretely, the semiconductor includes: titanium oxide, zinc oxide, tin oxide, ferric oxide, tungsten trioxide, dibismuth trioxide and strontium titanate.

From the above examples, the hydrophilic substance and the photo semiconductor have common substances. When using these substances, needless to say, a layer containing only the above substance that is a hydrophilic substance and a photo semiconductor, should be formed on a substrate surface.

Irradiating a UV uses a UV light source or sunray. The UV wavelength includes a short wavelength to a degree that the electron on a valence electron band in the photo semiconductor can be excited. For example, a 400 nm or less wavelength is used for titanium oxide. Any UV intensity can be used, but the experiments described later prove that at least a  $0.003 \text{ mW/cm}^2$  or more intensity has a photo hydrophilic effect sufficiently. Therefore, general indoor illumination like a white light fluorescent lamp can sufficiently be used for a UV light source. Of course, a light source that can irradiate a stronger UV such as a xenon lamp, BLB lamp, metal halide lamp and mercury lamp,

can also be used.

[0027]

The preferable embodiment of the present invention is comprised of methods of improving, maintaining and recovering the hydrophilicity of a member surface including the steps of: forming on a substrate surface a layer containing a hydrophilic substance, a photo semiconductor and an accumulated water substance, and irradiating thereon a UV.

The accumulated water substance refers to a substance that can accumulate water in a construction, and a silica compound is a type of it. In general, silica is used as a desiccant; and it is said that diffusion of water in amorphous silica cuts a Si-O-Si bond in a meshed construction, and is progressed by forming a Si-OH+HO-Si partially (J. Non-cryst. Solids, 73 (2), 197-204 (1985)). In this way, the amorphous silica absorbs water in the meshed construction.

[0028]

Next, the concrete example of a step of forming on a substrate surface a layer containing a hydrophilic substance like a metal oxide and a photo semiconductor like titanium oxide, is explained.

The step of forming a layer containing a substance that is a hydrophilic substance and a photo semiconductor, is first explained.

One method includes: the steps of applying to a substrate an organic metal compound including a metal element comprising the above substance, hydrolyzing and dehydrated-condensing the organic metal compound to obtain



an amorphous metal oxide, and crystallizing the amorphous metal oxide.

The organic metal compound includes metal alkoxide and metal complex. Because of being a heat-activated process, the crystallization can be realized, e.g. by heat treatment.

The applying step can use flow coating. The hydrolyzing may be performed by contacting moisture at the same time at the application, or may be heated later.

The dehydrated-condensing can be achieved by heating.

Still, to increase adherence to a substrate, an integrating agent comprised of an inorganic amorphous material like silica, may be provided between a substrate and a surface layer.

[0029]

Another method includes: the steps of applying to a substrate a sol of the above substance, and heat-calcining thereof.

Applying a sol can use spray coating and dip coating. In this case, to increase adhesion to a substrate, an integrating agent comprised of an inorganic amorphous material like silica and glaze, may be provided between a substrate and a surface layer.

A commercially available sol may be used, or a particle comprised of the above substance may be dispersed.

[0030]

Still another method includes the steps of: applying to a substrate a metal comprised of the above substance, and oxidizing and crystallizing the metal.

Applying the metal can use sputtering and deposited electron beam.

Oxidizing the metal can use electro-chemically anodic oxidation and heat oxidation in an atmosphere including atmospheric oxygen.

Because of being a heat-activated process, the crystallization can be realized, e.g. by heat treatment.

In the case where a substrate itself is a metal comprised of the above substance, needless to say, the step of applying metal can be omitted.

[0031]

Next, a method of forming a layer containing a photo semiconductor and a hydrophilic substance like an accumulated water substance other than a photo semiconductor, or a method of forming a layer containing 2 kinds or more photo semiconductors hydrophilic, is explained.

In this case, basically the same method as the above can be taken.

One method includes the steps of: mixing a sol comprised of 2 kinds or more of the above substances to apply thereof a substrate, and heating and calcining thereof.

Another method includes the steps of: applying to a substrate an organic metal compound including a metal element comprised of 2 kinds or more of the above substances, hydrolyzing 2 kinds or more of the above organic metal compounds to obtain an amorphous metal oxide, and crystallizing the amorphous metal oxide.

Still another method includes the steps of: applying to a substrate a metal comprised of 2 kinds or more of the above substances, and oxidizing and crystallizing the metal.

[0032]

Further, in the case where the above hydrophilic substance other than the photo semiconductor is a resin, the following method can be used.

In other words, it includes the steps of: mixing a photo semiconductor sol with a hydrophobic resin having a main chain with photo resistance like alkylalcoxysilane and a side chain hydrophobic decomposed with a UV to apply thereof to a substrate, curing the hydrophobic resin, and substituting by a photo semiconductor action at least the side chain hydrophobic in the hydrophobic resin on the substrate surface with a hydroxyl group.

The main chain having photo resistance refers to a highpolymer main chain that cannot be decomposed with a UV of the order of 300 - 400 nm, or is hard to be decomposed, and a Si-O bond is its type.

The side chain hydrophobic decomposed with a UV refers to a highpolymer side chain that can be decomposed with a UV of the order of 300 - 400 nm, and includes e.g. Si-R (R, an alkyl group), Si-A (A, a phenyl group), and Si-X (X, a halogen group).

Curing the hydrophobic resin can use methods such as dehydrated-condensation after hydrolyzing, and adding a cross-linking agent to produce cross-linked reaction. Alkylalcoxysilane, used for a start raw material, is hydrolyzed to generate alkylsilanol, and further is dehydrated-condensed to form a Si-O main chain.

In this case, the hydrolyzing can be made by moisture included at mixing with the photocatalytic sol, and by heating as necessary. The dehydrated-condensation can be

achieved by heating.

Substituting by a photo semiconductor action at least a side chain hydrophobic in the hydrophobic resin on the substrate surface with a hydroxyl group, can be e.g. by being subjected to a UV light with energy above the forbidden band width of the photocatalyst. In the case where alkylalcoxysilane is used for a start raw material, this step is used to substitute an alkyl group with a hydroxyl group for rendering the resin hydrophilic.

[0033]

The above method of rendering hydrophilic and methods of improving, maintaining and recovering the hydrophilicity, can be used for a wide variety of applications including: the body part of a vehicle such as an automobile, bicycle, motorcycle, tricycle, vehicle, airplane, lift, ropeway, cable car, helicopter, monorail, tractor, rice-planting machine, balloon, airship, bus, tanker and dump truck; a clothes pole, roof material such as a roof tile and slate; an building external wall and a tile thereof such as a roof, bridge, girder, rail, pedestrian overpass, overbridge, sound barrier of a highway, windowpane, general housing, building, station house, railcar barn, warehouse, shed, temporary housing and seaside clubhouse; external wall material such as a laminated steel and mortar, tower, chimney, outdoor art work, torii, monument such as a statue of Buddha and bronze statue, screen door, blade of wind power generation, facility of an amusement park, gravestone, antenna for sanitary, TV and PHS, automated outdoor camera, monitoring outdoor camera, signboard, traffic sign, plastic greenhouse, greenhouse, outdoor wall, nameplate, automobile wheel,

spoke, rim and wheel of a bicycle, door, emergency stairs, handrail guardrail, veranda, outdoor trash can, telephone booth, solar battery cover, parking lot, toll box of a toll road, roof pipe, tent, streetlight, outdoor speaker, outdoor exposed part of the deck of a passenger boat and tanker, traffic signal, bench, pavement, shutter, exterior of public lavatory, arcade, air conditioner, vending machine, post, mailbox, seat of a stadium, outdoor illumination, dome roof, high-voltage tower, scoreboard, neon, aurora vision, illumination, railroad, crossing, solar water heater, outdoor electric water heater, ad balloon, utility pole, discharging wall of a dam, outdoor tank, cooling tower, container, filler of a gas station, commercial open-air bathtub, rain shutter, reservoir, platform, pool, station yard, building stone paved for an artificial falls and fountain, tile, insulator, sealer between walls, zoo cage, vehicle cover, reflector, railroad signal sign, railroad bridge, fence, support, and automobile safe mirror.

According to the above methods, these things can be rendered hydrophilic, and improve, maintain and recover the hydrophilicity by forming on parts exposed outdoors thereof a layer including a photo semiconductor, and using a sunray UV, and thereby, can use flowing water in rain or normal use for self-cleaning.

[0034]

Another examples include: a tableware for general use, disaster, camping and pet, kitchen sink, ventilation fan, hood, fan, gas range, gas stove, cutting board, rice cooker, faucet, washstand, bathroom bench, bathtub, bathtub cover, hot water feeder, soap case, shower, washing machine, water

tank of a washing machine, floor, wall and ceiling of a bathroom, toilet, kitchen, living room, warehouse, medical room, unit bath and sauna, and inner wall material forming thereof such as a interior paper, tile, wood, laminated steel and building stone, sanitary ware, toilet, toilet cover, table, tablecloth, white board, heating plate, telephone, toy for babies and infants, barbecue set, tank for decorative fish and aquarium, drain tube of a business-application refrigerator, the surface of film coating machine, tube for circulating cooling water, animal keeping case or room such as a bird cage and kennel, filter of an air conditioner, the inside of a refrigerator, the inside of a microwave, musical instrument such as wind, stringed and percussion instruments, speaker, microphone, exhaust vent of a chimney, sash, curtain wall, windowpane, bolt, rail, sealer between walls, shade of lighting equipment, indoor illumination, pot of a decorative plant, inner wall of a tunnel, cleaning tool such as a dust cloth and mop, the inside of a vacuum cleaner, oil painting pallet, brush, jewelry such as an earring and ring, operating button, keyboard and switch such as appliance, lighting, audio and OA equipment, remote controller and telephone, door knob, handle, handrail, screen, eyeglasses, mirror of a bathroom and lavatory, dental mirror, shop's food case storing juice and frozen food, food transparent pack, and rain goggle. According to the above methods, these things can be rendered hydrophilic, and improve, maintain and recover the hydrophilicity by forming on the surface thereof a layer including a photo semiconductor, and using an indoor illumination or cleaning UV, and thereby,

can deliver cleaning facility only with water.

[0035]

Still another examples include: a mirror of a bathroom and lavatory, automobile safe mirror, dental mirror, shop's food case storing juice and frozen food, food transparent pack, vehicle window, eyeglasses, windowpane, rain goggle, showcase of a vending machine, window of an airport control tower, speedometer frame of a motorcycle, lens for a camera, telescope, microscope and photo etching, and traffic mirror. According to the above methods, these things can be rendered hydrophilic, and improve, maintain and recover the hydrophilicity by forming on the surface thereof a layer including a photo semiconductor, and using an indoor illumination, sunray or a UV light source for antifogging before use, and thereby, can deliver an antifogging effect.

[0036]

Yet another examples include: a solar battery, high-voltage power transmission line, heat exchanger, plastic greenhouse ceiling, airplane wing, snow country roof material, snow country rainwater pipe, and snow country antenna. According to the above methods, these things can be rendered hydrophilic, and improve, maintain and recover the hydrophilicity by forming on the surface thereof a layer including a photo semiconductor, and using an indoor illumination, sunray or a UV light source for antifogging before use, and thereby, can deliver an anticondensing effect. This can avoid the following points that: the droplet on a solar battery acts as a convex lens to cause heat damage; the droplet deposited on a high-voltage power transmission line is conical in shape for arc discharge to

cause power loss; the droplet deposited between the fins in a heat exchanger is frozen to cause lowered efficiency; the droplet condensed at a particular position on a plastic greenhouse ceiling is dropped to cause a crop root to be rotten; the droplet deposited on an airplane wing causes increased load during fly; the droplet on a snow country roof material increases the amount of snow around a droplet-deposited part; the droplet on a snow country rainwater pipe forms an icicle around a droplet-deposited part; and the droplet on a snow country antenna occurs communication failure due to an increase in the amount of snow around a droplet-deposited part.

[0037]

Also, a living body material with a hydrophilic surface provides well adaptability; conventionally a hydrophilic resin is used for a catheter and contact lens ("Surface Technology", vol. 46, No. 10 (1995)). The hydrophilic material according to the present invention has the hydrophilicity and maintaining and recovering effects thereof better than those of the conventional hydrophilic resin. Thus, it is thought that alternating these materials will produce a more excellent effect.

[0038]

Further, the favorable hydrophilicity allows a surface to be wet uniformly; therefore, it is expected that, for deposit of the same amount of water, the material is dried quickly compared with a hydrophobic surface. Using this characteristic, it is thought that the present invention can be used for shorted time for washing a vehicle body part, prevented microbiological growth in a bathroom, and



shortened time for forming an ice surface uniformly on a skating rink.

[0039]

[Example]

Example 1 (titanium oxide layer, hydrophilicity recovery, BLB, 0.24  $\mu$ m film thickness, Taki)

An ammonia peptization type titanium oxide sol (A-6 of Taki Kagaku, solute concentration of 6% by weight, average crystal diameter of 8 nm) was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 110 - 900°C to obtain a sample. The film thickness was 0.24  $\mu$ m. As shown in Fig. 17, the hydrophilicity of the sample immediately after calcining was below 20° at any temperature. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time. For comparison, a general glazed tile was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV likewise to measure a contact angle with water to irradiated time.

[0040]

As a result, as shown in Fig. 1, the general glazed tile showed no change, while the embodiment sample calcined at 110 - 800°C allowed the hydrophilicity to be recovered (improved) to less than 20° with the BLB lamp for over one hour. Also, the sample calcined at 900°C showed the tendency of recovering (improving) the hydrophilicity slightly compared with the glazed tile.

[0041]

The average crystal diameter of titanium oxide (A-6) in

the sample calcined at 110 - 900°C, is shown in Table 1. Consequently, the average crystal diameter at 900°C was grown to about 800 nm, and it is thought that this weakened the hydrophilicity recovering (improving) power. Therefore, it would be preferable that the average crystal diameter of titanium oxide that forms a member after calcining is less than 800 nm.

[0042]

Table 1

[0043]

Example 2 (titanium oxide layer, hydrophilicity recovery, BLB, 0.80  $\mu$ m film thickness, Taki)

The titanium oxide sol used in Example 1 was applied to a glazed tile surface of 15 cm square, and the tile was calcined at 110 - 900°C to obtain a sample. The film thickness was 0.80  $\mu$ m. As shown in Fig. 18, the hydrophilicity of the sample immediately after calcining was below 20° at any temperature. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time.

For comparison, a general luster tile was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV likewise to measure a contact angle with water to irradiated time.

[0044]

As a result, as shown in Fig. 2, the general luster tile showed no change, while the embodiment sample calcined at 110 - 800°C allowed the hydrophilicity to be recovered (improved) to less than 20° with the BLB lamp for over one

hour. Also, the sample calcined at 900°C showed the tendency of recovering (improving) the hydrophilicity to about 30°.

[0045]

Example 3 (titanium oxide layer, hydrophilicity recovery, BLB, 0.80  $\mu$ m film thickness, Ishihara)

An ammonia peptization type titanium oxide sol (STS-11 of Ishihara Sangyo, solute concentration of 35 % by weight, average crystal diameter of 17 nm) was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 110 - 1000°C to obtain a sample. The film thickness was 0.80  $\mu$ m. As shown in Fig. 19, the hydrophilicity of the sample immediately after calcining was below 30° at any temperature. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time.

[0046]

As a result, as shown in Fig. 3, the sample calcined at 110 - 900°C allowed the hydrophilicity to be recovered (improved) to less than 15° with the BLB lamp for over one hour.

Also, the average crystal diameter of titanium oxide (STS-11) in the sample calcined at 110 - 900°C is shown in Table 1. Consequently, it was evident that, although the average crystal diameter at 900°C was grown to about 300 nm, it showed favorable hydrophilicity recovery (improvement). Therefore, the average crystal diameter of titanium oxide that forms a member after calcining is at least 300 nm or less, showing the favorable hydrophilicity recovery.

[0047]

Example 4 (titanium oxide layer, hydrophilicity recovery, BLB, 0.12  $\mu$ m film thickness, Nissan Chemical Ind.)

A nitric acid peptization type titanium oxide sol (TA-15 of Nissan Chemical Ind., solute concentration of 10 % by weight, average crystal diameter of 12 nm) was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 110 - 800°C to obtain a sample. The film thickness was 0.12  $\mu$ m. As shown in Fig. 20, the hydrophilicity of the sample immediately after calcining was below 30° at any temperature. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time.

[0048]

As a result, as shown in Fig. 4, the sample calcined at 110 - 800°C allowed the hydrophilicity to be recovered (improved) to less than 15° with the BLB lamp for over one hour. Also, comparing Examples 1, 2 and 4 revealed the following 2 points.

(1) At least a film thickness of 0.12 - 0.80  $\mu$ m will, regardless of the film thickness, recover (improve) the hydrophilicity by UV irradiation.

(2) Using either of an alkaline peptization-form titanium oxide sol or an acidic peptization type titanium oxide sol, will recover (improve) the hydrophilicity by UV irradiation.

[0049]

Example 5 (effect of calcium)

The titanium oxide sol used in Example 3 was applied to

a glazed tile surface of 75 mm square, and was calcined at 800°C for one hour to form a titanium oxide thin film with a film thickness of 0.3  $\mu$ m. After that, the surface was subjected to a 0.3 g calcium nitrate water solution with a calcium metal concentration of 50  $\mu$ mol/g, and then to a 0.4 mW/cm<sup>2</sup> BLB lamp for 10 minutes. Calcium was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was 38°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 5, BLB lamp irradiation for about 0.2 days allowed the hydrophilicity to be improved (recovered) to about 5°.

Compared with Example 3, this result showed no reduction in a function due to calcium addition, such as an photocatalytically oxidative-decomposing action, but a slightly favorable tendency

[0050]

Example 6 (effect of potassium)

In a manner similar to Example 5, a titanium oxide thin film was formed on a glazed tile surface. After that, the surface was subjected to a 0.3 g potassium chloride water solution with a potassium metal concentration of 50  $\mu$ mol/g, and then to a 0.4 mW/cm<sup>2</sup> BLB lamp for 10 minutes. Potassium was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was 37°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus

irradiated time.

As a result, as shown in Fig. 6, BLB lamp irradiation for about 0.2 days allowed the hydrophilicity to be improved (recovered) to about 8°.

Compared with Example 3, this result showed no reduction in a function due to potassium addition, such as a photocatalytically oxidative-decomposing action, but a slightly favorable tendency

[0051]

Example 7 (effect of sodium)

In a manner similar to Example 5, a titanium oxide thin film was formed on a glazed tile surface. After that, the surface was subjected to a 0.3g sodium nitrate water solution with a sodium metal concentration of 50  $\mu$ mol/g, and then to a 0.4 mW/cm<sup>2</sup> BLB lamp for 10 minutes. Sodium was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was 37°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 7, BLB lamp irradiation for about 0.2 days allowed the hydrophilicity to be improved (recovered) to about 7°.

Compared with Example 3, this result showed no reduction in a function due to sodium addition, such as a photocatalytically oxidative-decomposing action, but a slightly favorable tendency

[0052]

Example 8 (effect of magnesium)

In a manner similar to Example 5, a titanium oxide thin film was formed on a glazed tile surface. After that, the surface was subjected to a 0.3g magnesium chloride di water salt water solution with a magnesium metal concentration of  $50 \mu\text{mol/g}$ , and then to a  $0.4 \text{ mW/cm}^2$  BLB lamp for 10 minutes. Magnesium was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was  $37^\circ$ . The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a  $0.3 \text{ mW/cm}^2$  UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 8, BLB lamp irradiation for about 0.2 days allowed to the hydrophilicity to be improved (recovered) to about  $8^\circ$ .

Compared with Example 3, this result showed no reduction in a function due to magnesium addition, such as a photocatalytically oxidative-decomposing action, but a slightly favorable tendency

[0053]

Example 9 (effect of lithium)

In a manner similar to Example 5, a titanium oxide thin film was formed on a glazed tile surface. After that, the surface was subjected to a 0.3 g lithium chloride water solution with a lithium metal concentration of  $50 \mu\text{mol/g}$ , and then to a  $0.4 \text{ mW/cm}^2$  BLB lamp for 10 minutes. Lithium was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was  $36^\circ$ . The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a  $0.3 \text{ mW/cm}^2$  UV to measure a change in a contact angle with water versus

irradiated time.

As a result, as shown in Fig. 9, BLB lamp irradiation for about 0.2 days allowed the hydrophilicity to be improved (recovered) to about 8°.

Compared with Example 3, this result showed no reduction in a function due to lithium addition, such as a photocatalytically oxidative-decomposing action, but a slightly favorable tendency

[0054]

Example 10 (effect of zinc)

In a manner similar to Example 5, a titanium oxide thin film was formed on a glazed tile surface. After that, the surface was subjected to a 0.3 g zinc chloride water solution with a zinc metal concentration of 50  $\mu\text{mol/g}$ , and then to a 0.4  $\text{mW/cm}^2$  BLB lamp for 10 minutes. Zinc was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was 43°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3  $\text{mW/cm}^2$  UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 10, BLB lamp irradiation for about 0.2 day allowed the hydrophilicity to be improved (recovered) to about 8°. Compared with Example 3, this result showed no reduction in a function due to zinc addition, such as a photocatalytically oxidative-decomposing action, but a slightly favorable tendency

[0055]

Example 11 (effect of strontium)

In a manner similar to Example 5, a titanium oxide thin



film was formed on a glazed tile surface. After that, the surface was subjected to a 0.3g strontium chloride hexa water salt water solution with a strontium concentration of 50  $\mu$  mol/g, and then to be subjected to a 0.4 mW/cm<sup>2</sup> BLB lamp for 10 minutes. Strontium was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was 33°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time. As a result, as shown in Fig. 11, BLB lamp irradiation for about 0.2 day allowed the hydrophilicity to be improved (recovered) to about 7°, showing a slightly favorable tendency compared with Example 3.

[0056]

#### Example 12 (effect of nickel)

In a manner similar to Example 5, a titanium oxide thin film was formed on a glazed tile surface. After that, the surface was subjected to a 0.3 g nickel chloride water solution with a nickel concentration of 50  $\mu$  mol/g, and then to a 0.4 mW/cm<sup>2</sup> BLB lamp for 10 minutes. Nickel was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was 41°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time. As a result, as shown in Fig. 12, BLB lamp irradiation for about 0.2 day allowed the hydrophilicity to be improved (recovered) to about 17°, showing the almost same value as that of Example 3.

[0057]

Example 13 (effect of platinum)

In a manner similar to Example 5, a titanium oxide thin film was formed on a glazed tile surface. After that, the surface was subjected to a 0.3 g  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  water solution with a platinum concentration of 50  $\mu\text{mol/g}$ , and then to a 0.4  $\text{mW/cm}^2$  BLB lamp for 10 minutes. Platinum was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was 42°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3  $\text{mW/cm}^2$  UV to measure a change in a contact angle with water versus irradiated time. As a result, as shown in Fig. 13, BLB lamp irradiation for about 0.2 day allowed the hydrophilicity to be improved (recovered) to about 6°, showing a slightly favorable tendency compared with Example 3.

[0058]

Example 14 (effect of palladium)

In a manner similar to Example 5, a titanium oxide thin film was formed on a glazed tile surface. After that, the surface was subjected to a 0.3 g palladium chloride water solution with a palladium concentration of 50  $\mu\text{mol/g}$ , and then to a 0.4  $\text{mW/cm}^2$  BLB lamp for 10 minutes. Palladium was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was 47°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3  $\text{mW/cm}^2$  UV to measure a change in a contact angle with water versus irradiated time. As a result, as shown in Fig. 14, BLB lamp irradiation for about 0.2 day allowed the hydrophilicity to

be improved (recovered) to about  $6^\circ$ , showing a slightly favorable tendency compared with Example 3.

[0059]

#### Example 15 (effect of iron)

In a manner similar to Example 5, a titanium oxide thin film was formed on a glazed tile surface. After that, the surface was subjected to a 0.3 g ferric chloride water solution with an iron concentration of  $50 \mu\text{mol/g}$ , and then to a  $0.4 \text{ mW/cm}^2$  BLB lamp for 10 minutes. Iron was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was  $51^\circ$ . The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a  $0.3 \text{ mW/cm}^2$  UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 15, BLB lamp irradiation for about 0.75 days allowed the hydrophilicity to be improved (recovered) to about  $12^\circ$ , showing the almost same value as that of Example 3.

[0060]

#### Example 16 (effect of silver)

In a manner similar to Example 5, a titanium oxide thin film was formed on a glazed tile surface. After that, the surface was subjected to a 0.3 g silver nitrate water solution with a silver concentration of  $50 \mu\text{mol/g}$ , and then to a  $0.4 \text{ mW/cm}^2$  BLB lamp for 10 minutes. Silver was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was  $40^\circ$ . The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a  $0.3 \text{ mW/cm}^2$  UV to measure

a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 16, BLB lamp irradiation for about 0.75 days allowed the hydrophilicity to be improved (recovered) to about  $14^\circ$ , showing the almost same value as that of Example 3.

[0061]

Example 17 (effect of copper)

In a manner similar to Example 5, a titanium oxide thin film was formed on a glazed tile surface. After that, the surface was subjected to a 0.3 g copper acetate mono water salt water solution with a copper concentration of  $50 \mu\text{mol/g}$ , and then to a  $0.4 \text{ mW/cm}^2$  BLB lamp for 10 minutes. Copper was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was  $72^\circ$ . The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a  $0.3 \text{ mW/cm}^2$  UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 21, BLB lamp irradiation for about 0.75 days allowed the hydrophilicity to be improved (recovered) to about  $22^\circ$ .

[0062]

Example 18 (A-6 sol of Taki,  $0.03 \text{ mW/cm}^2$ )

An ammonia peptization type titanium oxide sol (A-6 of Taki Kagaku, solute concentration of 6% by weight, average crystal diameter of 8 nm) was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at  $800^\circ\text{C}$  for one hour to obtain a sample. The film thickness was  $0.3 \mu\text{m}$ . The contact angle with

water of the sample immediately after calcining was 15'. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a  $0.03 \text{ mW/cm}^2$  UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 22, BLB lamp irradiation with such a weak UV intensity for about one day allowed the hydrophilicity to be improved (recovered) to about 19'.

[0063]

#### Example 19 (effect of alumina)

An anatase-form titanium oxide sol (A-6 of Taki Kagaku, solute concentration of 6% by weight, average crystal diameter of 8 nm) and a Bemite form aluminum oxide sol (Alumina sol-520 of Nissan Chemical Ind., solute concentration of 20 % by weight, specific surface area of  $250 \text{ m}^2/\text{g}$ ) were mixed to allow the molar ratio of solid content to be 88 : 12. The mixture was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at  $800^\circ\text{C}$  for one hour to obtain a sample. The film thickness was  $0.3 \text{ }\mu\text{m}$ . The hydrophilicity of the sample immediately after calcining was 10'. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a  $0.03 \text{ mW/cm}^2$  UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 23, the sample subjected to a BLB lamp irradiation with such a weak UV intensity for about one day, allowed the hydrophilicity to be recovered (improved) to about 15', and showed the recovery (improvement) slightly better than that of the sample coated only with titanium oxide, providing the possibility of using

indoor illumination as a light source. This result is greatly different from that of a photocatalytically oxidative-decomposing action that lowers a function due to addition of aluminum oxide.

[0064]

#### Example 20 (effect of zirconia)

An anatase-form titanium oxide sol (A-6 of Taki Kagaku, solute concentration of 6% by weight, average crystal diameter of 8 nm) and a zirconium oxide sol (NZS-30B of Nissan Chemical Ind., solute concentration of 30 % by weight) were mixed to allow the molar ratio of solid content to be 88 : 12. The mixture was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 800°C for one hour to obtain a sample. The film thickness was 0.3  $\mu$ m. The contact angle with water of the sample immediately after calcining was 23°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.03 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 24, the sample subjected to a BLB lamp irradiation with such a weak UV intensity for about one day allowed the hydrophilicity to be recovered (improved) to about 15°, and showed the recovery (improvement) slightly better than that of the sample coated only with titanium oxide, providing the possibility of using indoor illumination as a light source. This result is greatly different from that of a photocatalytically oxidative-decomposition action that lowers a function due to addition of zirconium oxide.

[0065]

Example 21 (effect of ceria)

An anatase-form titanium oxide sol (A-6 of Taki Kagaku, solute concentration of 6 % by weight, average crystal diameter of 8 nm) and a cerium oxide sol (W-15 of Taki Kagaku, solute concentration of 15 % by weight, average crystal diameter of 8 nm) were mixed to allow the molar ratio of solid content to be 88 : 12. The mixture was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 800°C for one hour to obtain a sample. The film thickness was 0.3  $\mu$ m. The contact angle with water of the sample immediately after calcining was 22°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.03 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 25, the sample subjected to a BLB lamp irradiation with such a weak UV intensity for about 2 days allowed the hydrophilicity to be recovered (improved) to about 15°, and showed the recovery (improvement) slightly better than that of the sample coated only with titanium oxide, providing the possibility of using indoor illumination as a light source.

[0066]

Example 22 (effect of tin oxide)

An anatase-form titanium oxide sol (A-6 of Taki Kagaku, solute concentration of 6% by weight, average crystal diameter of 8 nm) and a tin oxide sol (of Taki Kagaku, solute concentration of 10% by weight, average crystal diameter of 3.5 nm) were mixed to allow the molar ratio of

solid content to be 88 : 12. The mixture was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 800°C for one hour to obtain a sample. The film thickness was 0.3  $\mu$ m. The contact angle with water of the sample immediately after calcining was 10°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.03 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 26, the sample subjected to a BLB lamp irradiation with such a weak UV intensity for about one day allowed the hydrophilicity to be recovered (improved) to about 15°, and showed the recovery (improvement) slightly better than that of the sample coated only with titanium oxide, providing the possibility of using indoor illumination as a light source.

[0067]

Example 23 (effect of antimony-added tin oxide)

An anatase-form titanium oxide sol (A-6 of Taki Kagaku, solute concentration of 6% by weight, average crystal diameter of 8 nm) and an antimony-added tin oxide sol (Celamese G of Taki Kagaku, solute concentration of 10 % by weight, average crystal diameter of 25 nm) were mixed to allow the molar ratio of solid content to be 88 : 12. The mixture was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 800°C for one hour to obtain a sample. The film thickness was 0.3  $\mu$ m. The contact angle with water of the sample immediately after calcining was 10°. The obtained sample was kept in the dark for one week, and was subjected to a



BLB lamp with a  $0.03 \text{ mW/cm}^2$  UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 27, the sample subjected to a BLB lamp with such a weak UV intensity, allowed the hydrophilicity to be recovered (improved) to about  $15^\circ$  one day later, then to about  $12^\circ$  2 days later, and showed the recovery (improvement) slightly better than that of the sample coated only with titanium oxide, providing the possibility of using indoor illumination as a light source.  
[0068]

Example 24 (STS-11 sol of Ishihara,  $0.03 \text{ mW/cm}^2$ )

An ammonia peptization anatase-form titanium oxide sol (STS-11 of Ishihara Sangyo, solute concentration of 35% by weight, average crystal diameter of 17 nm) was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at  $800^\circ\text{C}$  for one hour to obtain a sample. The film thickness was  $0.3 \mu\text{m}$ . The contact angle with water of the sample immediately after calcining was  $9^\circ$ . The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a  $0.03 \text{ mW/cm}^2$  UV to measure a change in a contact angle with water versus irradiated time. As a result, as shown in Fig. 28, the sample subjected to a BLB lamp with such a weak UV intensity, allowed the hydrophilicity to be recovered (improved) to about  $15^\circ$  one day later, then to about  $12^\circ$  2 days later, providing the possibility of using indoor illumination as a light source.

[0069]

Example 25 (effect of alkali peptization type silica sol)

An ammonia peptization type anatase-form titanium oxide

sol (STS-11 of Ishihara Sangyo, solute concentration of 35% by weight, average crystal diameter of 17 nm) and a colloidal silica sol (Snowtex 20 of Nissan Chemical Ind., solute concentration of 20 % by weight, average crystal diameter of 15 nm, pH 9.7) were mixed to allow the molar ratio of solid content to be 88 : 12. The mixture was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 800°C for one hour to obtain a sample. The film thickness was 0.3  $\mu$ m. The contact angle with water of the sample immediately after calcining was 5°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.03 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 29, when the sample was kept in the dark for one week, the contact angle with water was not increased so much and was held at 9°. Also, the sample subjected to a BLB lamp with such a weak UV intensity for about one day, was rendered super-hydrophilic (or resulted in improved hydrophilicity) to 0°, providing the possibility of using indoor illumination as a light source.

[0070]

Example 26 (effect of acid peptization type silica sol)

An ammonia peptization type anatase-form titanium oxide sol (STS-11 of Ishihara Sangyo, solute concentration of 35% by weight, average crystal diameter of 17 nm) and a colloidal silica sol (Snowtex 0 of Nissan Chemical Ind., solute concentration of 20% by weight, average crystal diameter of 15 nm, pH 3) were mixed to allow the molar ratio of solid content to be 88 : 12. The mixture was applied to

a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 800°C for one hour to obtain a sample. The film thickness was 0.3  $\mu\text{m}$ . The contact angle with water of the sample immediately after calcining was 5°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.03  $\text{mW}/\text{cm}^2$  UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 30, when the sample was kept in the dark for one week, the contact angle with water was not changed and was held at 5°. Also, the sample subjected to a BLB lamp with such a weak UV intensity for about one day, was rendered super-hydrophilic (or resulted in improved hydrophilicity) to 0°, providing the possibility of using indoor illumination as a light source.

[0071]

Example 27 (CS-N of Ishihara, 0.03  $\text{mW}/\text{cm}^2$ )

A nitric acid peptization type anatase-form titanium oxide sol (CS-N of Ishihara Sangyo, solute concentration of 30 % by weight, average crystal diameter of 7 nm, pH 1.5) was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 800°C for one hour to obtain a sample. The film thickness was 0.3  $\mu\text{m}$ . The contact angle with water of the sample immediately after calcining was 21°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.03  $\text{mW}/\text{cm}^2$  UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 31, the sample subjected to a BLB lamp with such a weak UV intensity for about one

day, allowed the hydrophilicity to be recovered (improved) to about 12°, providing the possibility of using indoor illumination as a light source.

[0072]

Example 28 (effect of yttrium)

An anatase-form titanium oxide sol (CS-N of Ishihara Sangyo, solute concentration of 30% by weight, average crystal diameter of 7 nm, pH 1.5) and an acetic acid peptization type yttrium oxide sol (Taki Kagaku, solute concentration of 15% by weight, average crystal diameter of 4 nm, pH 7.6) were mixed to allow the molar ratio of solid content to be 88 : 12. The mixture was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 800°C for one hour to obtain a sample. The film thickness was 0.3  $\mu$ m. The contact angle with water of the sample immediately after calcining was 21°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.03 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 32, the sample subjected to a BLB lamp with such a weak UV intensity for about 2 days, allowed the hydrophilicity to be improved (recovered) to about 10°, and showed the hydrophilicity slightly better than that of the sample coated only with titanium oxide, providing the possibility of using indoor illumination as a light source.

[0073]

Example 29 (CS-C of Ishihara, 0.03 mW/cm<sup>2</sup>)

A hydrochloric acid peptization type anatase-form

titanium oxide sol (CS-C of Ishihara Sangyo, solute concentration of 30 % by weight, average crystal diameter of 7 nm, pH 1.5) was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 800°C for one hour to obtain a sample. The film thickness was 0.3  $\mu$ m. The contact angle with water of the sample immediately after calcining was 23°. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.03 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 33, the sample subjected to a BLB lamp with such a weak UV intensity for about one day, allowed the hydrophilicity to be improved (recovered) to about 14°, providing the possibility of using indoor illumination as a light source.

[0074]

Example 30 (STS-11 sol of Ishihara, hydrophilicity maintenance under indoor illumination) An ammonia peptization type anatase-form titanium oxide sol (STS-11 of Ishihara Sangyo, solute concentration of 35% by weight, average crystal diameter of 17 nm, pH 11.5) was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 110 - 800°C for one hour to obtain a sample. The film thickness was 0.24  $\mu$ m. The contact angle with water of the sample immediately after calcining is shown in Fig. 34. After being kept in the dark for one week, the obtained sample was subjected to a BLB lamp at 0.3 mW/cm<sup>2</sup> for one week, and then at 0.1 mW/cm<sup>2</sup> for one more week to be sufficiently rendered hydrophilic. After that, the sample was subjected to a white light

fluorescent lamp with a  $0.003 \text{ mW/cm}^2$  UV to check the hydrophilicity maintenance under indoor illumination.

As a result, as shown in Fig. 35, the sample calcined at any temperature maintained the hydrophilicity 9 days later, providing the possibility of using practically indoor illumination as a light source.

[0075]

Example 31 (hydrophilicity maintenance under indoor illumination, added platinum)

In a manner similar to Example 5, a titanium oxide thin film was formed on a glazed tile surface. After that, the surface was subjected to a  $0.3\text{g H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  water solution with a platinum metal concentration of  $50 \mu\text{mol/g}$ , and then to a  $0.4 \text{ mW/cm}^2$  BLB lamp for 10 minutes. Platinum was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was  $18^\circ$ . After being kept in the dark for one week, the obtained sample was subjected to a BLB lamp at  $0.3 \text{ mW/cm}^2$  for one week, and then at  $0.1 \text{ mW/cm}^2$  for one more week to be sufficiently rendered hydrophilic. After that, the sample was subjected to a white light fluorescent lamp with a  $0.01 \text{ mW/cm}^2$  UV to check the hydrophilicity maintenance under indoor illumination.

As a result, as shown in Fig. 36, the sample maintained the hydrophilicity 9 days later, providing the possibility of using indoor illumination as a light source.

[0076]

Example 32 (hydrophilicity maintenance under indoor illumination, added palladium)

In a manner similar to Example 5, a titanium oxide thin

film was formed on a glazed tile surface. After that, the surface was subjected to a 0.3 g palladium chloride water solution with a palladium metal concentration of  $50 \mu\text{mol/g}$ , and then to a  $0.4 \text{ mW/cm}^2$  BLB lamp for 10 minutes. Palladium was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was  $22^\circ$ . After being kept in the dark for one week, the obtained sample was subjected to a BLB lamp at  $0.3 \text{ mW/cm}^2$  for one week, and then at  $0.1 \text{ mW/cm}^2$  for one more week to be sufficiently rendered hydrophilic. After that, the sample was subjected to a white light fluorescent lamp with a  $0.01 \text{ mW/cm}^2$  UV to check the hydrophilicity maintenance under indoor illumination.

As a result, as shown in Fig. 37, the sample maintained the hydrophilicity 9 days later, providing the possibility of using indoor illumination as a light source.

[0077]

#### Example 33 (effect of ruthenium)

In a manner similar to Example 5, a titanium oxide thin film was formed on a glazed tile surface. After that, the surface was subjected to a 0.3 g ruthenium chloride water solution with a ruthenium metal concentration of  $50 \mu\text{mol/g}$ , and then to a  $0.4 \text{ mW/cm}^2$  BLB lamp for 10 minutes. Ruthenium was fixed on the substrate to obtain a sample. The contact angle with water of the sample immediately after calcining was  $26^\circ$ . After being kept in the dark for one week, the obtained sample was subjected to a BLB lamp at  $0.3 \text{ mW/cm}^2$  to measure a change in the contact angle with water versus irradiated time.

As a result, as shown in Fig. 38, the sample allowed

the hydrophilicity to be improved (recovered) to  $16^{\circ}$  0.4 days later and  $12^{\circ}$  1.2 days later.

[0078]

Example 34 (hydrophilicity maintenance under indoor illumination, added silica sol)

An ammonia peptization type anatase-form titanium oxide sol (STS-11 of Ishihara Sangyo, solute concentration of 35 % by weight, average crystal diameter of 17 nm) and a colloidal silica sol (Snowtex 20 of Nissan Chemical Ind., solute concentration of 20% by weight, average crystal diameter of 15 nm, pH 9.7) were mixed to allow the molar ratio of solid content to be 80 : 20. The mixture was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at  $800^{\circ}\text{C}$  for one hour to obtain a sample. The film thickness was  $0.3\ \mu\text{m}$ . The contact angle with water of the sample immediately after calcining was  $5^{\circ}$ . The obtained sample was kept in the dark for 2 weeks, and was subjected to a white light fluorescent lamp with a  $0.004\ \text{mW}/\text{cm}^2$  UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 39, when the sample was kept in the dark for 2 weeks, the contact angle with water was not increased so much and was held at  $14^{\circ}$ . Also, the sample subjected to a BLB lamp with such a weak UV intensity for about one day, was rendered super-hydrophilic (or resulted in improved hydrophilicity) to  $4^{\circ}$ , providing the possibility of using practically indoor illumination as a light source.

[0079]

Example 35 (tin oxide sol of 15% by weight + effect of added



silver, 750°C)

An ammonia peptization type anatase-form titanium oxide sol (STS-11 of Ishihara Sangyo, solute concentration of 35% by weight, average crystal diameter of 17 nm) and a tin oxide sol (of Taki Kagaku, solute concentration of 10% by weight, average crystal diameter of 3.5 nm) were mixed so that a ratio by weight of the tin oxide solid content versus the sum of the solid contents of the titanium oxide and tin oxide was 15 %. The mixture of 0.03 g was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 750°C for 10 minutes. Then, the surface was subjected to a silver nitrate water solution of 1% by weight, and to a 0.4 mW/cm<sup>2</sup> BLB lamp for 10 minutes. Silver was fixed on the substrate to obtain a sample. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 40, 48 hours later, the sample allowed the contact angle with water to reach 0°, and was rendered super-hydrophilic (or resulted in improved hydrophilicity).

[0080]

Example 36 (tin oxide sol of 50% by weight + effect of added silver, 750°C)

An ammonia peptization type anatase-form titanium oxide sol (STS-11 of Ishihara Sangyo, solute concentration of 35% by weight, average crystal diameter of 17 nm) and a tin oxide sol (of Taki Kagaku, solute concentration of 10% by weight, average crystal diameter of 3.5 nm) were mixed so

that a ratio by weight of the tin oxide solid content versus the sum of the solid contents of the titanium oxide and tin oxide was 50%. The mixture of 0.03g was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 750°C for 10 minutes. Then, the surface was subjected to a silver nitrate water solution of 1% by weight, and to a 0.4 mW/cm<sup>2</sup> BLB lamp for 10 minutes. Silver was fixed on the substrate to obtain a sample. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 41, 24 hours later, the sample allowed the contact angle with water to be less than 5°, and 144 hours later, to be 0°, and was rendered super-hydrophilic (or resulted in improved hydrophilicity).

[0081]

Example 37 (tin oxide sol of 100 % by weight + effect of added silver, 750°C)

A tin oxide sol (of Taki Kagaku, solute concentration of 10% by weight, average crystal diameter of 3.5 nm) was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 750°C for 10 minutes. Then, the surface was subjected to a silver nitrate water solution of 1 % by weight, and then to a 0.4 mW/cm<sup>2</sup> BLB lamp for 10 minutes. Silver was fixed on the substrate to obtain a sample. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time. As a result, as shown in Fig. 42, the sample allowed the hydrophilicity to be

gradually improved (recovered), and 72 hours later, the contact angle with water, to be less than  $10^\circ$ .

[0082]

Example 38 (tin oxide sol of 5% by weight + effect of added silver,  $800^\circ\text{C}$ )

An ammonia peptization type anatase-form titanium oxide sol (STS-11 of Ishihara Sangyo, solute concentration of 35% by weight, average crystal diameter of 17 nm) and a tin oxide sol (of Taki Kagaku, solute concentration of 10 % by weight, average crystal diameter of 3.5 nm) were mixed so that a ratio by weight of the tin oxide solid content versus the sum of the solid contents of the titanium oxide and tin oxide was 5%. The mixture of 0.03 g was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at  $800^\circ\text{C}$  for 10 minutes. Then, the surface was subjected to a silver nitrate water solution of 1 % by weight, and to a  $0.4 \text{ mW/cm}^2$  BLB lamp for 10 minutes. Silver was fixed on the substrate to obtain a sample. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a  $0.3 \text{ mW/cm}^2$  UV to measure a change in a contact angle with water versus irradiated time. As a result, as shown in Fig. 43, 24 hours later, the sample allowed the contact angle with water to reach  $0^\circ$ , and was rendered super-hydrophilic (or resulted in improved hydrophilicity).

[0083]

Example 39 (tin oxide sol of 1% by weight,  $800^\circ\text{C}$ )

An ammonia peptization type anatase-form titanium oxide sol (STS-11 of Ishihara Sangyo, solute concentration of 35 % by weight, average crystal diameter of 17 nm) and a tin

oxide sol (of Taki Kagaku, solute concentration of 10% by weight, average crystal diameter of 3.5 nm) were mixed so that a ratio by weight of the tin oxide solid content versus the sum of the solid contents of the titanium oxide and tin oxide was 5%. The mixture of 0.03 g was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 800°C for 10 minutes to obtain a sample. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water versus irradiated time.

As a result, as shown in Fig. 44, the sample allowed the contact angle with water to be less than 5° 24 hours later, and to reach 0° 120 hours later, and was rendered super-hydrophilic (or resulted in improved hydrophilicity).

[0084]

Example 40 (tin oxide sol of 95% by weight, 800°C)

An ammonia peptization type anatase-form titanium oxide sol (STS-11 of Ishihara Sangyo, solute concentration of 35% by weight, average crystal diameter of 17 nm) and a tin oxide sol (of Taki Kagaku, solute concentration of 10 % by weight, average crystal diameter of 3.5 nm) were mixed so that a ratio by weight of the tin oxide solid content versus the sum of the solid contents of the titanium oxide and tin oxide was 95 %. The mixture of 0.03 g was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 800°C for 10 minutes to obtain a sample. The obtained sample was kept in the dark for one week, and was subjected to a BLB lamp with a 0.3 mW/cm<sup>2</sup> UV to measure a change in a contact angle with water

versus irradiated time.

As a result, as shown in Fig. 45, 48 hours later, the sample allowed the contact angle with water to be less than  $10^\circ$ , and the hydrophilicity to be improved (recovered).

[0085]

Example 41 (hydrophilicity maintenance under indoor illumination, added tin oxide)

An ammonia peptization type anatase-form titanium oxide sol (STS-11 of Ishihara Sangyo, solute concentration of 35% by weight, average crystal diameter of 17 nm) and a tin oxide sol (Taki Kagaku, solute concentration of 10% by weight, average crystal diameter of 3.5 nm) were mixed to allow the molar ratio of solid content to be 88 : 12. The mixture was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at  $800^\circ\text{C}$  for one hour to obtain a sample. The film thickness was  $0.3\text{ }\mu\text{m}$ . The contact angle with water of the sample immediately after calcining was  $6^\circ$ . After being kept in the dark for 2 weeks, the obtained sample was subjected to a BLB fluorescent lamp with a  $0.3\text{ mW/cm}^2$  UV for 13 days to allow the contact angle with water to be  $0^\circ$ , and further was subjected to a white light fluorescent lamp with a  $0.004\text{ mW/cm}^2$  UV to measure a time-varying change in a contact angle with water under the weak irradiation.

As a result, as shown in Fig. 46, 2 days later, the sample allowed the contact angle to be held at less than  $10^\circ$ , providing the possibility of using practically indoor illumination as a light source.

[0086]

Example 42 (hydrophilicity maintenance under indoor

illumination, added tin oxide of added antimony)

An anatase-form titanium oxide sol (A-6 of Taki Kagaku, solute concentration of 6% by weight, average crystal diameter of 8 nm) and a tin oxide sol of added antimony (Celamese G of Taki Kagaku, solute concentration of 10% by weight, average crystal diameter of 25 nm) were mixed to allow the molar ratio of solid content to be 88 : 12. The mixture was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 800°C for one hour to obtain a sample. The film thickness was 0.3  $\mu$ m. The contact angle with water of the sample immediately after calcining was 6°. After being kept in the dark for 2 weeks, the obtained sample was subjected to a BLB fluorescent lamp with a 0.3 mW/cm<sup>2</sup> UV for 13 days to allow the contact angle with water to be 0°, and further was subjected to a white light fluorescent lamp with a 0.004 mW/cm<sup>2</sup> UV to measure a time-varying change in a contact angle with water under the weak irradiation.

As a result, as shown in Fig. 47, 4 days later, the sample allowed the contact angle to be held at 6° or less, providing the possibility of using practically indoor illumination as a light source.

[0087]

Example 43 (hydrophilicity maintenance under indoor illumination, added yttrium)

A nitric acid peptization type anatase-form titanium oxide sol (CS-N of Ishihara Sangyo, solute concentration of 30 % by weight, average crystal diameter of 7 nm, pH 1.5) and an acetic acid peptization type yttrium oxide sol (of Taki Kagaku, solute concentration of 15% by weight, average

crystal diameter of 4 nm, pH 7.6) were mixed to allow the molar ratio of solid content to be 88 : 12. The mixture was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 800°C for one hour to obtain a sample. The film thickness was 0.3  $\mu$ m. The contact angle with water of the sample immediately after calcining was 21°. After being kept in the dark for 2 weeks, the obtained sample was subjected to a BLB fluorescent lamp with a 0.3 mW/cm<sup>2</sup> UV for 13 days to allow the contact angle with water to be 2°, and further was subjected to a white light fluorescent lamp with a 0.004 mW/cm<sup>2</sup> UV to measure a time-varying change in a contact angle with water under the weak irradiation.

As a result, as shown in Fig. 48, 4 days later, the sample allowed the contact angle to be held at less than 10°, providing the possibility of using practically indoor illumination as a light source.

[0088]

Example 44 (hydrophilicity maintenance under indoor illumination, added alumina)

A hydrochloric acid peptization type anatase-form titanium oxide sol (CS-C of Ishihara Sangyo, solute concentration of 30% by weight, average crystal diameter of 7 nm, pH 1.5) and an amorphous aluminum oxide sol (Alumina sol-100 of Nissan Chemical Ind., solute concentration of 10% by weight, specific surface area of 400 m<sup>2</sup>/g, pH 3.5) were mixed to allow the molar ratio of solid content to be 88 : 12. The mixture was applied to a glazed tile surface of 15 cm square by a spray coating method, and the tile was calcined at 800°C for one hour to obtain a sample. The film

thickness was 0.3  $\mu\text{m}$ . The contact angle with water of the sample immediately after calcining was  $2^\circ$ . After being kept in the dark for 2 weeks, the obtained sample was subjected to a BLB fluorescent lamp with a  $0.3\text{ mW/cm}^2$  UV for 13 days to allow the contact angle with water to be  $2^\circ$ , and further was subjected to a white light fluorescent lamp with a  $0.004\text{ mW/cm}^2$  UV to measure a time-varying change in a contact angle with water under the weak irradiation.

As a result, as shown in Fig. 49, 2 days later, the sample allowed the contact angle to be held at less than  $10^\circ$ , providing the possibility of using practically indoor illumination as a light source.

[0089]

Example 45 (effect of the molar fraction of silica)

An ammonia peptization type anatase-form titanium oxide sol (STS-11 of Ishihara Sangyo, solute concentration of 35% by weight, average crystal diameter of 17 nm) and a colloidal silica sol (Snowtex 20 of Nissan Chemical Ind., solute concentration of 20% by weight, average crystal diameter of 15 nm, pH 9.7) were mixed at a ratio by weight of 100 : 0, 95 : 5, 90 : 10, 85 : 15, 80 : 20, 75 : 25 and 70 : 30. Each of the mixtures were applied to a glazed tile surface of 15 cm square by a spray coating method. The applied amount thereof was 0.08g. After that, the tiles were calcined at  $800^\circ\text{C}$  for one hour to obtain a sample.

The contact angles of the samples immediately after calcining are as shown in Fig. 50. Therefore, forming on a substrate surface a mixed layer of titanium oxide and silica, shows a rather favorable hydrophilicity immediately after production.



Further, the obtained samples were kept in the dark for 8 days. The contact angles of the samples are as shown in Fig. 51. Comparing this result with Fig. 51, it was apparent that the increased rate of the contact angle of the sample that forms a mixed layer of titanium oxide and silica on a substrate surface and is kept in the dark, is rather lower than that of the sample coated only with titanium oxide.

Further, the samples were subjected to a BLB lamp with a  $0.03 \text{ mW/cm}^2$  UV for 2 days to improve their hydrophilicity. The contact angles of the samples are shown in Fig. 52. Compared this result with Figs. 50 and 51, it proved that all the samples lowered the contact angles with water; especially, all the samples that form a mixed layer of titanium oxide and silica on a substrate surface were rendered hydrophilic (or resulted in improved hydrophilicity) to about  $0^\circ$ .

Furthermore, the samples were left in the dark for 8 days to check hydrophilicity maintenance thereof. The contact angles of the samples are shown in Fig. 53. Compared this result with Figs. 50 and 51, it proved that all the samples with silica of 5 - 25% by mol maintained the favorable hydrophilicity from the start and in the dark.

[0090]

Each of the wear resistance of the samples was checked. Slided wearing with a plastic eraser was performed, and changes in an appearance were compared for evaluation. The evaluating indexes are shown below.

◎: No change in 40 slidings.

○: 10 or more and less than 40 slidings caused a surface

layer to be scratched and peeled off.

△: 5 or more and less than 10 slidings caused a surface layer to be scratched and peeled off.

×: Less than 5 slidings caused a surface layer to be scratched and peeled off.

As a result, all the samples mentioned above showed ◎, a favorable result. Further, each of the surface hardness of the samples was checked. The surface hardness was evaluated with a hardness wherein a member surface was scratched with a pencil with different hardnesses of 6B - 9H to produce scoring. The results are shown in Fig. 54. As a result, it was apparent that the sample that forms a mixed layer of titanium oxide and silica on the substrate surface, can have the surface hardness more excellent than that of the sample coated only with titanium oxide.

[0091]

Example 46 (effect of UV wavelength)

The sample used in Example 24 was kept in the dark for 10 days to make a sample. With a Hg-Xe lamp and single color UV of the condition in Table 2, a time-varying change in the contact angles with water of the sample and a comparing sample (glazed tile). The results are shown in Fig. 55 (a) - (c). As a result, as shown in Fig. 55 (c), it was evident that the samples subjected to a UV with a 405 nm wavelength having energy lower than the forbidden band width of anatase-form titanium oxide, hardly improved the hydrophilicity, but as shown in Fig. 55 (a) and (b), the samples subjected to UVs with 365 nm and 313 nm wavelengths having energy higher than the forbidden band width of anatase-form titanium oxide, improved the hydrophilicity.

Thus, it proved that a characteristic of anatase-form titanium oxide as a photo semiconductor, contributes greatly to improved hydrophilicity.

[0092]

Table 2

[0093]

Example 47 (sputtering method)

A metal titanium film was formed on a soda glass substrate by a sputtering method, and the substrate was calcined at 500°C to obtain a sample. An anatase-form titanium oxide crystal was observed on the obtained sample surface. Upon being calcined, the sample surface was constantly subjected to a 0.5 mW/cm<sup>2</sup> BLB lamp to measure a time-varying change in a contact angle with water. The results are shown in Fig. 56. The diagram revealed that the sample allowed the contact angle with water to be kept less than 3°, and maintained the hydrophilicity, when a photo semiconductor containing layer was formed by the sputtering method.

[0094]

Example 48 (atmospheric oxidizing method, rutile)

A metal titanium plate surface was heat-treated with a gas burner at about 1100°C to form thereon an oxidatively coated layer containing a rutile-form titanium oxide crystal. After being left for several months, the sample was constantly subjected to a 0.5 mW/cm<sup>2</sup> BLB lamp to measure a time-varying change in a contact angle with water. The results are shown in Fig. 57. According to the diagram, the sample subjected to the irradiation for over 2 hours,

allowed the hydrophilicity to be improved and recovered to less than  $20^\circ$ , and then was constantly subjected to the UV to maintain the hydrophilicity.

Thus, the following points are concluded.

- (1) It was shown that the sample on which a photo semiconductor containing layer is formed by an atmospheric oxidizing method, is rendered hydrophilic to be maintained.
- (2) It was shown that the sample coated with rutile-form titanium oxide that has almost no effect in photocatalytically oxidative decomposition, can deliver the photo hydrophilic effect.

[0095]

Example 49 (anode oxidizing method)

An amorphous titanium oxide layer was formed on a metal titanium plate surface by an anode oxidizing method, and was heat-treated to crystallize titanium oxide. After being left for several months, the sample was subjected to a  $0.5 \text{ mW/cm}^2$  BLB lamp to measure a time-varying change in a contact angle with water. The results are shown in Fig. 58. According to the diagram, the sample subjected to the irradiation, allowed the hydrophilicity to be improved and recovered to  $20^\circ$  2 hours later, and to  $10^\circ$  4 hours later. Thus, it was shown that the sample on which a photo semiconductor containing layer is formed by an anode oxidizing method, is rendered hydrophilic.

[0096]

Example 50 (atmospheric oxidizing method, anatase)

Metal titanium plates were atmospherically calcined at  $650^\circ\text{C}$ ,  $700^\circ\text{C}$ ,  $750^\circ\text{C}$  and  $800^\circ\text{C}$  in an electric furnace to obtain samples. An oxidatively coated layer containing an

anatase-form titanium oxide crystal was formed on the surface of each sample. After being left in the dark for one week, the samples were subjected to a  $0.5 \text{ mW/cm}^2$  BLB lamp to measure contact angles with water 24 hours later. The results are shown in Fig. 59. The diagram revealed that the samples treated at any calcined temperature, allowed the hydrophilicity to be improved (recovered) to less than  $20^\circ$ . Thus, it was shown that the sample on which an anatase-form titanium oxide containing layer is formed by an atmospherically oxidizing method, allows the hydrophilicity to be improved (recovered).

[0097]

Example 51 (applied anatase powder,  $0.5 \text{ mW/cm}^2$ )

An anatase-form titanium oxide powder (of Nihon Aerosol K.K., P 25 powder) was added and mixed in a liquid in which a silane coupling agent was diluted with ethanol. The mixture was applied to a soda glass plate surface to be dried. The sample surface was subjected to a  $0.5 \text{ mW/cm}^2$  BLB lamp to measure a time-varying change in a contact angle with water. The results are shown in Fig. 60. The diagram revealed that the contact angle with water was kept at less than  $10^\circ$ , and the sample subjected to slurried powders, can be rendered hydrophilic to be maintained.

[0098]

Example 52 (applied anatase powder,  $0.01 \text{ mW/cm}^2$ )

An anatase-form titanium oxide powder (of Nihon Aerosol K.K., P25 powder) was added and mixed in a liquid in which a silane coupling agent was diluted with ethanol. The mixture was applied to a soda glass plate surface to be dried. The sample surface was subjected to a  $0.01 \text{ mW/cm}^2$  white light

fluorescent lamp to measure a time-varying change in a contact angle with water. The results are shown in Fig. 61. The diagram revealed that the contact angle with water was improved to less than 20° by one-hour irradiation, and the sample subjected to slurried powders, can be rendered hydrophilic.

[0099]

Example 53 (titanium containing chelate method, 7 nm film thickness, 0.01 mW/cm<sup>2</sup>)

A soda glass plate surface was subjected to titanium containing chelate, and was calcined at 500°C to form a surface layer containing an anatase-form titanium oxide crystal. The surface layer film thickness of the obtained sample was 7 nm. The sample surface was subjected to a 0.5 mW/cm<sup>2</sup> BLB lamp for one hour, and then to 0.01 mW/cm<sup>2</sup> white light fluorescent lamp to measure a time-varying change in a contact angle with water. The results are shown in Fig. 62. The diagram revealed that the contact angle with water was kept at 0° under the white light fluorescent lamp.

Thus, the following point are concluded.

- (1) It was shown that the sample on which an anatase-form titanium oxide containing layer was formed by an organic chelate method, is rendered hydrophilic to be maintained.
- (2) It was shown that the sample with a thin film of 7 nm is rendered hydrophilic to be maintained. This characteristic is extremely important to apply to a transparent material like glass.

[0100]

Example 54 (titanium containing chelate method, 20 nm film thickness, 0.01 mW/cm<sup>2</sup>)

A soda glass plate surface was subjected to titanium containing chelate, and was calcined at 500°C to form a surface layer containing an anatase-form titanium oxide crystal. The surface layer film thickness of the obtained sample was 20 nm. The sample surface was subjected to a 0.5 mW/cm<sup>2</sup> BLB lamp for one hour, and then to 0.01 mW/cm<sup>2</sup> white light fluorescent lamp to measure a time-varying change in a contact angle with water. The results are shown in Fig. 63. The diagram revealed that the contact angle with water was kept at 0° under the white light fluorescent lamp.

[0101]

Example 55 (alkoxide method, effect of calcining temperature)

First, silicon alkoxide was coated on a soda glass plate surface of 10 cm square. The silicon alkoxide was coated by the method below. First, tetraethoxysilane, 36 % hydrochloric acid, pure water and ethanol were mixed at a ratio of 6 : 2 : 6 : 86 (weight ratio). At this point, the heated mixture was left for about an hour.

After that, this was flow-coated to the soda glass plate surface. Next, titanium alkoxide was coated thereon. The titanium alkoxide was coated by the method below. First, tetraethoxytitanium and ethanol were mixed at a ratio of 1 : 9 (weight ratio). To control the hydrolyzed speed, the 36 % hydrochloric acid of 10 % by weight versus the tetraethoxytitanium was added to the mixture. Then, in the dry air, this solution was flow-coated on the above silicon alkoxide layer. The coated amount was 45  $\mu$ g/cm<sup>2</sup> by converting into titanium oxide.

Next, the solution was dried for 1 - 10 minutes to

promote hydrolyzing and dehydrated condensation of the titanium alkoxide layer and silicon alkoxide layer to form an amorphous titanium oxide layer and a silica layer. After that, after being calcined at 450°C, 475°C, 500°C and 525°C, the plates were subjected to a 0.5 mW/cm<sup>2</sup> BLB lamp for 3 hours to obtain samples. The obtained samples were constantly subjected to a white light fluorescent lamp with a 0.02 mW/cm<sup>2</sup> UV to measure a time-varying change in a contact angle with water. Still, anatase-form crystalline titanium oxide was observed at 475°C, 500°C, and 525°C by powder X-ray diffraction, but was not observed at 450°C.

[0102]

Table 3

[0103]

The results are shown in Table 3. The table proved that the samples are rendered super-hydrophilic (or resulted in improved hydrophilicity) to 0° at 475°C, 500°C and 525°C at which crystalline titanium oxide was observed, and maintains the hydrophilicity as long as subjected to a white light fluorescent lamp.

Also, the photocatalytically oxidative decomposition of the sample calcined at 500°C, was checked. The sample surface was subjected to oleic acid glycerido, and then to a BLB lamp of 1.1 mW/cm<sup>2</sup> UV to check a change in weight before and after the irradiation. The results are shown in Fig. 80. The diagram shows no reduction in weight after the irradiation; it was proved that the photocatalytically oxidative decomposition of this sample is extremely weak. Therefore, the hydrophilic phenomenon in the sample would



not be based on a photocatalytic action.

[0104]

Example 56 (the relation between UV irradiation and the amount of physically absorbed water)

Three anatase-form titanium oxide powders (by Nihon aerosol K.K., P-25) were pressed in disk-shape. The following 3 experiments (A) - (C) thereof were performed, respectively. To measure IR (infrared spectroscopy) in these experiments, FT-IR (Fourier transformation type infrared spectrometer, FTS-40A) was used. Also, a used UV lamp (UVL-21) is a type irradiating a UV with a 366 nm wavelength.

Also, the IR spectrum diagram shown later, shows that a sharp absorption band of  $3690\text{ cm}^{-1}$  is stretched OH bond by chemically-absorbed water to the sample surface; a broad absorption band of  $3300\text{ cm}^{-1}$  is stretched OH bond by physically-absorbed water to the sample surface; a sharp absorption band of  $1640\text{ cm}^{-1}$  is bent HOH bond by physically absorbed water to the sample surface; and absorption bands of  $1700\text{ cm}^{-1}$ ,  $1547\text{ cm}^{-1}$ ,  $1475\text{ cm}^{-1}$ ,  $1440\text{ cm}^{-1}$  and  $1365\text{ cm}^{-1}$  are adhered carbonate (stain component) on the sample surface.

[0105]

Experiment (A): First, IR measurement for a disk immediately after press was performed (1 in Figs. 64 and 65). Next, the disk was stored for 17 hours in a dry box containing a silica gel as a desiccant to perform the IR measurement (2 in Figs. 64 and 65). The disk was placed in an air containing room, and then subjected to a UV ( $0.5\text{ mW/cm}^2$ ) for one hour to perform the IR measurement (3 in

Figs. 64 and 65, 1 in Figs. 66 and 67). The disk was stored for 24 hours in an air-containing dark room to perform the IR measurement (2 in Figs. 66 and 67). Last, the disk was subjected to a UV ( $0.5 \text{ mW/cm}^2$ ) again for one hour to perform the IR measurement (3 in Figs. 66 and 67).

As a result, the amounts of chemically absorbed water and physically absorbed water of the disk after stored in the dry box, were both decreased (1 to 2 in Figs. 64 and 65). In the meantime, the adhered amount of carbonate was increased (1 to 2 in Fig. 65). Also, the contact angle with water in this operation was increased from the above example.

Next, when the disk was subjected to a UV, the physically absorbed water was increased to be recovered to its original condition (2 to 3 in Figs. 64 and 65); the chemically absorbed water was also increased to be recovered to its considerably original condition (2 to 3 in Fig. 64); and the adhered amount of carbonate was decreased (2 to 3 in Fig. 65). The contact angle with water in this operation was decreased from the above example. Then, when the disk was stored for 24 hours in an air-containing dark room, the amounts of the chemically absorbed water and the physically absorbed water were both decreased slightly (1 to 2 in Figs. 66 and 67).

In the meantime, the adhered amount of carbonate was increased (1 to 2 in Fig. 66).

The contact angle with water in this operation was increased from the above example. Last, when the disk was subjected a UV again, the amount of the chemically absorbed water was unchanged (2 to 3 in Fig. 67); but the amount of

the physically absorbed water was increased (2 to 3 in Figs. 66 and 67). In the meantime, the adhered amount of carbonate was increased (2 to 3 in Fig. 66). The contact angle with water in this operation was decreased from the above example.

[0106]

Experiment (B): First, IR measurement for a disk immediately after press was performed (1 in Figs. 68 and 69). Next, the disk was subjected to a UV ( $0.5 \text{ mW/cm}^2$ ) for one hour to perform the IR measurement (2 in Figs. 68 and 69). The disk was subjected to a UV ( $0.5 \text{ mW/cm}^2$ ) for one more hour (total 2 hours) to perform the IR measurement (3 in Figs. 68 and 69). Further, the disk was subjected to a UV ( $0.5 \text{ mW/cm}^2$ ) for one more hour (total 3 hours), and then 2 more hours (total 5 hours) to perform the IR measurement. As a result, when the disk was subjected to a UV for the first time, the amounts of chemically absorbed water and physically absorbed water, were both increased (1 to 2 in Figs. 68 and 69). In the meantime, the adhered amount of carbonate was slightly increased (1 to 2 in Fig. 68). Also, the contact angle with water in this operation was decreased from the above example.

Next, when the disk was subjected to a UV for one more hour (total 2 hours), the chemically absorbed water was slightly decreased (2 to 3 in Fig. 69); the physically absorbed water was unchanged (2 to 3 in Figs. 68 and 69). In the meantime, the adhered amount of carbonate was slightly increased (2 to 3 in Fig. 68). The contact angle with water in this operation was maintained, i.e. unchanged from the above example. It is thought that because of being

saturated, the amount of the physically absorbed water was unchanged.

Then, when the disk was subjected to a UV for one more hour (total 3 hours), the chemically absorbed water was slightly decreased; the physically absorbed water was unchanged. In the meantime, the adhered amount of carbonate was increased. The contact angle with water in this operation was maintained, i.e. unchanged from the above example.

Further, when the disk was subjected to a UV for 2 more hours (total 5 hours), the chemically absorbed water was slightly decreased; the physically absorbed water was unchanged. In the meantime, the adhered amount of carbonate was increased. The contact angle with water in this operation was maintained, i.e. unchanged from the above example.

[0107]

Experiment (C): First, IR measurement for a disk immediately after press was performed (1 in Figs. 70 and 71). Next, the disk was stored for 34 hours in an air-containing dark room to perform the IR measurement (2 in Figs. 70 and 71). The disk was subjected to a UV ( $0.024 \text{ mW/cm}^2$ ) for 2 hours to perform the IR measurement (3 in Figs. 70 and 71).

As a result, after the disk was left in the air-containing dark room, the amounts of chemically absorbed water and the physically absorbed water were both decreased (1 to 2 in Figs. 70 and 71). In the meantime, the adhered amount of carbonate was increased (1 to 2 in Fig. 70). The contact angle with water in this operation was increased

from the above example.

Next, when the disk was subjected to a UV for 2 hours, the chemically absorbed water was slightly increased (2 to 3 in Fig. 71); the physically absorbed water was increased to be recovered to its original condition (2 to 3 in Figs. 70 and 71). In the meantime, the adhered amount of carbonate was slightly increased (2 to 3 in Fig. 70). The contact angle with water in this operation was decreased from the above example.

[0108]

Table 4

[0109]

The above experimental results are summarized in Table 4. In Table 4, a change in the contact angle with water corresponds well to a change in the physically absorbed water; that is, when the physically absorbed water was increased, the contact angle with water was decreased to improve the hydrophilicity.

The adhered amount of carbonate does not correspond well to a change in the contact angle with water; it was observed that the longer the disk is left in the air, the more the amount is increased. In spite that the adhered amount of carbonate is increased, the contact angle with water on a member surface subjected to a UV is decreased, i.e., to improve the hydrophilicity.

Further, as described later, the member surface subjected to a UV will easily deliver the stain resistance only by rainfall and water cleaning. It is understood that when a physically absorbed water layer is formed and

maintained on the member surface as the adhered amount of carbonate is increased, the presence of the layer can effectively prevent adhesion of carbonate to the member surface from being interfered.

In addition, in the results of Example 46, the physically absorbed water layer is caused to be formed by a photo semiconductor action.

It is apparent from the above experimental results and consideration, that a photocatalytic action such as oxidative decomposition, deodorizing and antibacterial properties of conventional organic stain, and the photo hydrophilic effect in the present invention, are different the essential actions. It is common that their starting points result from the photo semiconductor action. Based on the action, the conventional photocatalytic action generates active oxygen that causes oxidative decomposing and antibacterial actions. On the contrary, the photo hydrophilic effect that requires no active oxygen, causes the photo semiconductor action to directly generate a physically absorbed water layer, to show self-cleaning and cleaning facility.

[0110]

Example 57 (silicon resin method, effect of film thickness to a hydrophilic process)

The silica content in a silica sol (Glaska A of Japan Synthetic Rubber Co.) and net trimethoxymethylsilane (Glaska B of Japan Synthetic Rubber Co.) were mixed at a ratio by weight of 3 : 1. The liquid with the total solute concentration of 20 % by weight, was applied to an aluminum substrate of 10 cm square. Then, the substrate was

thermoset at 150°C to form thereon a resin layer of 5  $\mu$ m film thickness.

The above silica sol was added to an anatase-form titanium oxide sol (TA-15 of Nissan Chemical Ind., solute concentration of 10 % by weight) and was diluted with ethanol. The solution to which the above trimethoxymethylsilane was added, was applied on the above resin layer. After that, the layer was thermoset at 150°C to form mixed layers with various film thicknesses. The ratio by weight of the titanium oxide solid content versus the sum of the solid contents (resin) of the silica and trimethoxymethylsilane and the titanium oxide solid content, was 50 %.

[0111]

The above mixed layer formations were subjected to a 0.5 mW/cm<sup>2</sup> BLB lamp to be rendered hydrophilic. Changes in the contact angles with water in this process are shown in Fig. 72. All the samples with any of film thicknesses was rendered hydrophilic to 0°. This hydrophilic phenomenon is essentially different from the photo hydrophilic effect as described so far. In other words, a large amount of methyl groups resulting from a siloxane resin, are exposed on a substrate surface before this hydrophilic process, to show the hydrophobicity. The phenomenon is a process from this condition to reaction substituting the methyl groups with hydroxyl groups.

Also, this phenomenon is different essentially from the conventional photocatalytically oxidative decomposition. Two examples are shown as follows.

[0112]

The oxidative decomposition of methylmercaptan for the above sample, is shown in Fig. 73. R30 of the vertical axis in the diagram shows a decomposed rate of methylmercaptan wherein the methylmercaptan was placed in a 11L desiccator with the above sample, to be subjected to a BLB lamp ( $0.6 \text{ mW/cm}^2 \text{ UV}$ ) for 30 minutes. The diagram shows clear film thickness dependence for the oxidative decomposition of methylmercaptan; the R30 for the sample with a  $0.5 \text{ }\mu\text{m}$  or less film thickness, is less than 20%, showing almost no decomposition.

Fig. 74 is a diagram showing oil decomposition for the above samples with  $0.03 \text{ }\mu\text{m}$  and  $0.2 \text{ }\mu\text{m}$  film thicknesses. The vertical axis in the diagram shows a change in weight per unit area, at applying oleic acid glyceride on the samples, and then at irradiating a BLB lamp of  $1.1 \text{ mW/cm}^2 \text{ UV}$  by keeping 76% humidity on the sample surface. Therefore, a decrease in this weight shows that the photocatalytically oxidative decomposition is progressed. However, Fig. 74 shows no decrease in weight, and the photocatalytically oxidative decomposition is not progressed at all.

[0113]

The phenomenon at the above hydrophilic process is thought to be as follows at present. In Example 55, a photo semiconductor particle subjected to a UV increases initially chemically absorbed water; thus, a hydroxyl group is chemically absorbed on the photo semiconductor particle by UV irradiation. The hydroxyl group chemically absorbed is adjacent to the alkyl group (a methyl group in this example) on a siloxane resin. Then, the hydroxyl group, a strong



nucleophilic agent, attacks the carbon of the alkyl group being adjacent, combining with the alkyl group to be released from a member surface. At the same time, active oxygen is generated in its surroundings by the photocatalytic action of the photo semiconductor particle, so that this active oxygen is combined with a Si free radical after the alkyl group is cut off from Si by the hydroxyl group, to generate a Si-O on the surface. The Si-O bond is essentially hydrophilic and has a semiconductor around this; physically absorbed water is formed on this Si-O bond by the photo hydrophilic effect, finally providing 0° level hydrophilicity. Therefore, the reaction of this hydrophilic process that uses part of the photocatalytic action, does not produce the reaction of oxidative decomposition directly by the active oxygen generated. It has low dependence on film thickness, and progresses the reaction even with a film thickness such that the reaction of oxidative decomposition is not produced.

[0114]

Example 58 (silicon resin method, hydrophilicity maintenance)

The sample with a 0.1  $\mu\text{m}$  film thickness that was rendered hydrophilic in Example 57, was left in the dark for 2 weeks to check a contact angle with water. As a result, the contact angle with water was still 0°, proving maintained hydrophilicity.

[0115]

Example 59 (silicon resin method, self-cleaning)

In a manner similar to Example 57, a siloxane resin layer, followed by a mixed layer of titanium oxide and a

siloxane resin were formed on an aluminum substrate. The film thickness of the mixed layer of titanium oxide and a siloxane resin, was  $0.1 \mu\text{m}$ . This sample was placed in the sample mounted part of the apparatus shown in Fig. 75. The apparatus was set on the roof of a 5-story building, to evaluate a contact angle with water and self-cleaning, as time elapses.

The self-cleaning was evaluated by comparing a time-varying change in adhesion of a black, vertical pattern of stain with that of comparing samples. The time-varying change in adhesion of a black, vertical pattern of stain, was evaluated by a difference in color difference depending on a visual check and the place in the same sample (a difference in color difference between a much stain part (a part with a vertical pattern of stain) and a less stain part (a part without a vertical pattern of stain)). The color difference for a standard sample (a sample before subjected to a sunray) was measured with a color difference meter. Further, the specific glossiness for a sample before subjected to a sunray was found with a glossiness meter. The incidence angle was  $60^\circ$ . Still, used for the comparing samples are: sample A wherein only a siloxane resin layer was formed on the aluminum substrate, and Sample B wherein a silicon resin was applied to a calcium silicate plate.

[0116]

The time-varying change in a contact angle with water is shown in Fig. 76. The diagram proves that this embodiment sample was rendered hydrophilic to  $0^\circ$  within one day in a sunray to be maintained over 10 months. Also, this shows that the hydrophilicity can sufficiently be maintained

without constant UV irradiation, although the sample was hardly subjected to a UV at night.

Also, the adhesion of a black, vertical pattern of stain one week later, is shown in Fig. 77; that one month later, in Fig. 78. In the diagrams, the width of color difference shows the color difference between a part without a vertical pattern of stain and a part with a vertical pattern of stain. Also, the minimum value of the color difference data shows adhesion of a part without a vertical pattern of stain. In Fig. 77, one week later, a vertical pattern of stain of contrast corresponding to the color difference width of 3 in the comparing samples A and B, was already observed. In the embodiment sample, the width was less than 1, and a vertical pattern of stain was not observed visually. Also, the width of the adhesion of the part without a vertical pattern of stain was held within 1 in all the samples, and the embodiment sample had the most favorable result.

Also, in Fig. 78, one month later, a vertical pattern of stain of contrast corresponding to the color difference width of 3 in the comparing sample A, and that of 5 in the comparing sample B, were observed. In the embodiment sample, the width was less than 1, and a vertical pattern of stain was not observed visually. Also, the embodiment sample had the most favorable result in the adhesion of the part without a vertical pattern of stain, that was held within 1.

A change in the glossiness ratio by outdoor leaving is shown in Fig. 79. According to the diagram, 3 months later, the glossiness ratio was lowered to 0.52 in the comparing

sample A; the ratio was a favorable result of 0.95 or more in the embodiment sample.

[0117]

Example 60 (silicon resin method, cleaning facility)

In a manner similar to Example 57, a siloxane resin layer, followed by a mixed layer of titanium oxide and a siloxane resin were formed on an aluminum substrate. The film thickness of the mixed layer of titanium oxide and a siloxane resin, was 0.1  $\mu$ m. The above sample was placed in a box containing a BLB lamp, and was subjected to 0.3 mW/cm<sup>2</sup> intensity to be left for 3 hours. The sample surface was rendered hydrophilic to 0°.

After that, the above sample was taken out, and further was subjected to the oleic acid in a dropper to be left for 5 minutes. Then, this sample was immersed in the water such that the member was horizontal. The contact angle with oleic acid was increased to form a droplet which was floated up soon.

It is thought that the reason why this phenomenon occurred was that the sample surface was rendered hydrophilic to 0°, allowing water molecules that conform to the sample surface far more easily than the oleic acid to be burrowed between the sample surface and oleic acid in the water. Using the above phenomenon, the member is thought to be cleaned well only with water.

Also, for the purposes of comparison, the comparing samples A and B used in Example 58, were subjected to the oleic acid to be left for 5 minutes. Then, a test wherein the samples were immersed in the water so that the member is horizontal, was conducted. However, the oleic acid was not

floated up unlike the above embodiment sample. Besides it, oil scrubbed with fingers remained on the sample surface to be spreaded.

[0118]

Example 61 (Alkoxide method, antifogging)

The antifogging of the samples that maintained the hydrophilicity in Example 55, was checked by a breathing method, resulting in no fogging at all.

[0119]

[Effect of the Invention]

The present invention forms on a substrate surface a layer containing a hydrophilic substance and a photo semiconductor, so as to irradiate a UV thereon. The amount of physically absorbed water that is absorbed on a member surface, is increased to improve the hydrophilicity. Also, the surface formed by said method is subjected to a UV as necessary, so that a physically absorbed water layer is maintained to keep the hydrophilicity. Being stored in the dark for a long period, the surface formed by the above method deteriorates the hydrophilicity once, but is subjected to a UV to increase the physically absorbed water layer to recover the hydrophilicity. The level of the above hydrophilicity shows a value far better than that (about 50°) of a conventional hydrophilic resin, and may reach 0°. Further, unlike a conventional tile and glass, the member simply subjected to a UV is provided with effects that maintains and recovers the hydrophilicity. The order of intensity of a sunray or indoor illumination is enough for the above UV.

[Brief Description of the Drawings]

Fig. 1

It is a diagram showing the effect of calcined temperature to the improved hydrophilicity in Example 1 according to the present invention.

Fig. 2

It is a diagram showing the effect of calcined temperature to the improved hydrophilicity in Example 2 according to the present invention.

Fig. 3

It is a diagram showing the effect of calcined temperature to the improved and recovered hydrophilicity in Example 3 according to the present invention.

Fig. 4

It is a diagram showing the effect of calcined temperature to the improved and recovered hydrophilicity in Example 4 according to the present invention.

Fig. 5

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 5 according to the present invention.

Fig. 6

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 6 according to the present invention.

Fig. 7

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 7 according to the present invention.

Fig. 8

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 8 according to the present invention.

Fig. 9

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 9 according to the present invention.

Fig. 10

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 10 according to the present invention.

Fig. 11

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 11 according to the present invention.

Fig. 12

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 12 according to the present invention.

Fig. 13

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 13 according to the present invention.

Fig. 14

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 14 according to the present invention.

Fig. 15

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 15 according to the present invention.

Fig. 16

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 16 according to the present invention.

Fig. 17

It is a diagram showing the contact angle with water of the sample immediately after calcining in Example 1 according to the present invention.

Fig. 18

It is a diagram showing the contact angle with water of the sample immediately after calcining in Example 2 according to the present invention.



Fig. 19

It is a diagram showing the contact angle with water of the sample immediately after calcining in Example 3 according to the present invention.

Fig. 20

It is a diagram showing the contact angle with water of the sample immediately after calcining in Example 4 according to the present invention.

Fig. 21

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 17 according to the present invention.

Fig. 22

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 18 according to the present invention.

Fig. 23

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 19 according to the present invention.

Fig. 24

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 20 according to the present invention.

Fig. 25

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 21 according to the present invention.

Fig. 26

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 22 according to the present invention.

Fig. 27

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 23 according to the present invention.

Fig.28

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 24 according to the present invention.

Fig. 29

It is a diagram showing the performances of the maintained, improved and recovered hydrophilicity in Example 25 according to the present invention.

Fig. 30

It is a diagram showing the performances of the maintained, improved and recovered hydrophilicity in Example 26 according to the present invention.

Fig. 31

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 27 according to the present invention.

Fig. 32

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 28 according to the present invention.

Fig. 33

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 29 according to the present invention.

Fig. 34

It is a diagram showing the contact angle with water of the sample immediately after calcining in Example 30 according to the present invention.

Fig. 35

It is a diagram showing the performance of the maintained hydrophilicity in Example 30 according to the present invention.

Fig. 36

It is a diagram showing the performance of the maintained hydrophilicity in Example 31 according to the present invention.

Fig. 37

It is a diagram showing the performance of the maintained hydrophilicity in Example 32 according to the present invention.

Fig. 38

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 33 according to the present invention.

Fig. 39

It is a diagram showing the performances of the maintained, improved and recovered hydrophilicity in Example 34 according to the present invention.

Fig. 40

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 35 according to the present invention.

Fig. 41

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 36 according to the present invention.

Fig. 42

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 37 according to the present invention.

Fig. 43

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 38 according to the present invention.

Fig. 44

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 39 according to the present invention.

Fig. 45

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 40 according to the present invention.

Fig. 46

It is a diagram showing the performance of the maintained hydrophilicity in Example 41 according to the present invention.

Fig. 47

It is a diagram showing the performance of the maintained hydrophilicity in Example 42 according to the present invention.

Fig. 48

It is a diagram showing the performance of the maintained hydrophilicity in Example 43 according to the present invention.

Fig. 49

It is a diagram showing the performance of the maintained hydrophilicity in Example 44 according to the present invention.

Fig. 50

It is a diagram showing the contact angle with water of the sample immediately after calcining in Example 45 according to the present invention.

Fig. 51

It is a diagram showing the contact angle with water of the sample after being left in the dark for 8 days in Example 45 according to the present invention.

Fig. 52

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 45 according to the present invention.

Fig. 53

It is a diagram showing the performance of the maintained hydrophilicity in Example 45 according to the present invention.

Fig. 54

It is a diagram showing the surface hardness in Example 45 according to the present invention.

Fig. 55

It is a diagram showing the effect of the UV wavelength of the performances of the improved and recovered hydrophilicity in Example 46 according to the present invention. (a) 313 nm, (b) 365 nm and (c) 405nm.

Fig. 56

It is a diagram showing the performance of the maintained hydrophilicity in Example 47 according to the present invention.

Fig. 57

It is a diagram showing the performances of the maintained, improved and recovered hydrophilicity in Example 48 according to the present invention.

Fig. 58

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 49 according to the present invention.

Fig. 59

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 50 according to the present invention.

Fig. 60

It is a diagram showing the performance of the maintained hydrophilicity in Example 51 according to the present invention.

Fig. 61

It is a diagram showing the performances of the improved and recovered hydrophilicity in Example 52 according to the present invention.

Fig. 62

It is a diagram showing the performance of the maintained hydrophilicity in Example 53 according to the present invention.

Fig. 63

It is a diagram showing the performance of the maintained hydrophilicity in Example 54 according to the present invention.

Fig. 64

It is a diagram showing the infrared spectroscopy spectrum related to Experiment (A) in Example 56 according to the present invention.

- 1: a disk immediately after press,
- 2: after stored in a dry box for 17 hours,
- 3: after being subjected to a  $0.5 \text{ mW/cm}^2$  UV for one hour.

Fig. 65

It is a diagram showing the infrared spectroscopy spectrum related to Experiment (A) in Example 56 according to the present invention.

- 1: a disk immediately after press,
- 2: after stored in a dry box in the dark for 17 hours,
- 3: after being subjected to a  $0.5 \text{ mW/cm}^2$  UV for one hour.



Fig. 66

It is a diagram showing the infrared spectroscopy spectrum related to Experiment (A) in Example 56 according to the present invention.

- 1: after being subjected to a  $0.5 \text{ mW/cm}^2$  UV for one hour,
- 2: after stored in the air in the dark for 24 hours,
- 3: after being re-subjected to a  $0.5 \text{ mW/cm}^2$  UV for one hour.

Fig. 67

It is a diagram showing the infrared spectroscopy spectrum related to Experiment (A) in Example 56 according to the present invention.

- 1: after being subjected to a  $0.5 \text{ mW/cm}^2$  UV for one hour,
- 2: after stored in the air in the dark for 24 hours,
- 3: after being re-subjected to a  $0.5 \text{ mW/cm}^2$  UV for one hour.

Fig. 68

It is a diagram showing the infrared spectroscopy spectrum related to Experiment (B) in Example 56 according to the present invention.

- 1: a disk immediately after press,
- 2: after being subjected to a  $0.5 \text{ mW/cm}^2$  UV for one hour,
- 3: after being subjected to a  $0.5 \text{ mW/cm}^2$  UV for one more hour (total 2 hours).

Fig. 69

It is a diagram showing the infrared spectroscopy spectrum related to Experiment (B) in Example 56 according to the present invention.

- 1: a disk immediately after press,
- 2: after being subjected to a  $0.5 \text{ mW/cm}^2$  UV for one hour,
- 3: after being subjected to a  $0.5 \text{ mW/cm}^2$  UV for one more hour (total 2 hours).

Fig. 70

It is a diagram showing the infrared spectroscopy spectrum related to Experiment (C) in Example 56 according to the present invention.

- 1: a disk immediately after press,
- 2: after stored in the air in the dark for 34 hours,
- 3: after being subjected to a  $0.024 \text{ mW/cm}^2$  UV for 2 hours.

Fig. 71

It is a diagram showing the infrared spectroscopy spectrum related to Experiment (C) in Example 56 according to the present invention.

- 1: a disk immediately after press,
- 2: after stored in the air in the dark for 34 hours,
- 3: after being subjected to a  $0.024 \text{ mW/cm}^2$  UV for 2 hours.

Fig. 72

It is a diagram showing the relation between the film thickness and hydrophilic process time in the mixed layer in Example 57 according to the present invention.

Fig. 73

It is a diagram showing the relation between the film thickness and deodorizing in the mixed layer in Example 57 according to the present invention.

Fig. 74

It is a diagram showing the oxidative decomposition of oil in Example 57 according to the present invention.

Fig. 75

It is a diagram showing the outdoor leaving test apparatus in Example 59 according to the present invention (the length unit is millimeter).

Fig. 76

It is a diagram showing the hydrophilic process and maintenance at outdoor leaving in Example 59 according to the present invention.

Fig. 77

It is a diagram showing the stain-resistance (self-cleaning) at outdoor leaving for one week in Example 59 according to the present invention.

Fig. 78

It is a diagram showing the stain-resistance (self-cleaning) at outdoor leaving for one month in Example 59 according to the present invention.

Fig. 79

It is a diagram showing the maintenance characteristic of glossiness ratio at outdoor leaving in Example 59 according to the present invention.

Fig. 80

It is a diagram showing the oxidative decomposition of oil in Example 55 according to the present invention.

Table 1

Temperature (°C)	A-6 (nm)	STS-11 (nm)
110	8	17
400	18	18
700	12	21
800	36	35
900	800	380
1000	—	>1000

Table 2

Wavelength (nm)	Intensity (mW/cm <sup>2</sup> )	Photon density (photon/sec/cm <sup>2</sup> )
313	10.6	$1.66 \times 10^{16}$
365	18.0	$3.31 \times 10^{16}$
405	6.0	$3.31 \times 10^{16}$

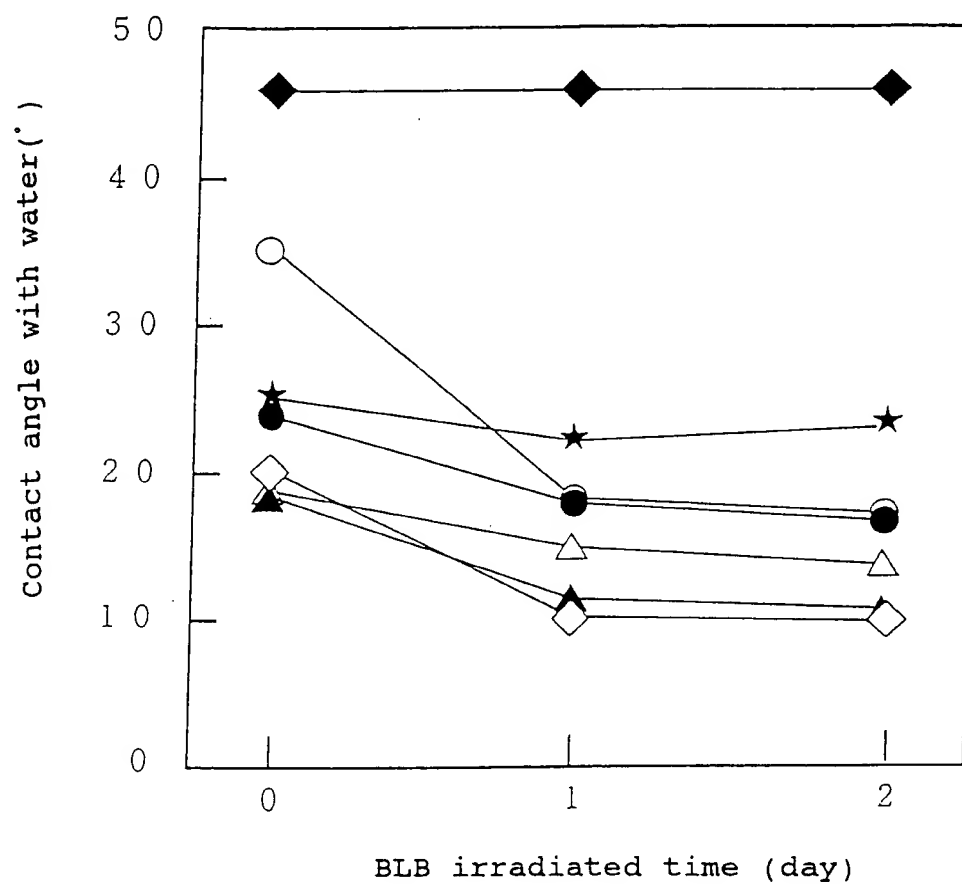
Table 3

Calcining temperature (°C)	Immediately after BLB irradiation (°)	3 days later (°)	9 days later (°)	14 days later (°)
450	10	13	15	23
475	0	0	0	0
500	0	0	0	0
525	0	0	0	0

Table 4

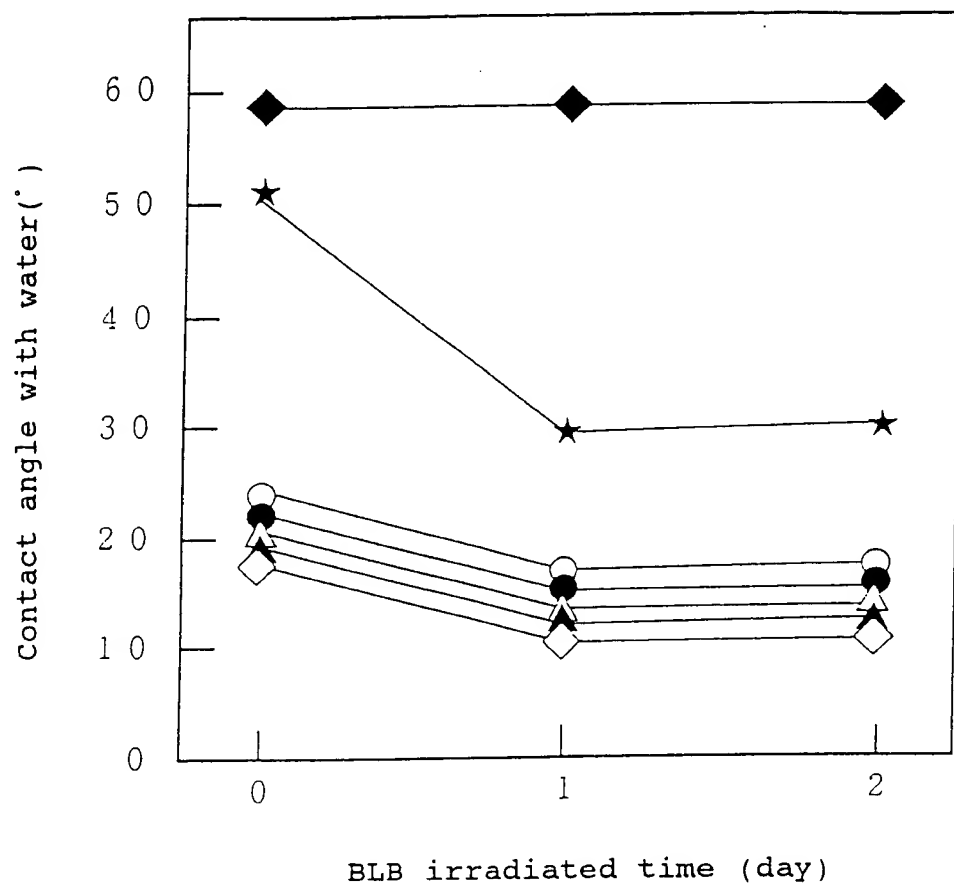
Experimental operation	Contact angle with water	Physically absorbed water	Chemically absorbed water	Adhered carbonate
A 0.5 mW/cm <sup>2</sup> UV (1 → 2) Be stored in the dark (dry) (2 → 3) Be subjected to a UV (dry) (1 → 2) Be stored in the dark (in the air) (2 → 3) Be subjected to a UV (in the air)	↑	↓	↓	↑
	↓	↑	↑	↓
	↑	↓	↓	↑
	↓	↑	→	↑
B 0.5 mW/cm <sup>2</sup> UV (1 → 2) Be subjected to a UV (1h) (2 → 3) Be subjected to a UV (2h) Be subjected to a UV (3h) Be subjected to a UV (5h)	↓	↑	↑	↑
	→	→	↓	↑
	→	→	↓	↑
	→	→	↓	↑
C 0.024 mW/cm <sup>2</sup> UV (1 → 2) Be stored in the dark (in the air) (2 → 3) Be subjected to a UV	↑	↓	↓	↑
	↓	↑	↑	↑

(↑ : Increase, ↓ Decrease, → Unchanged)



- ★ 900°C
- 800°C
- 700°C
- △ 600°C
- ▲ 400°C
- ◇ 110°C
- ◆ Only glazed tile

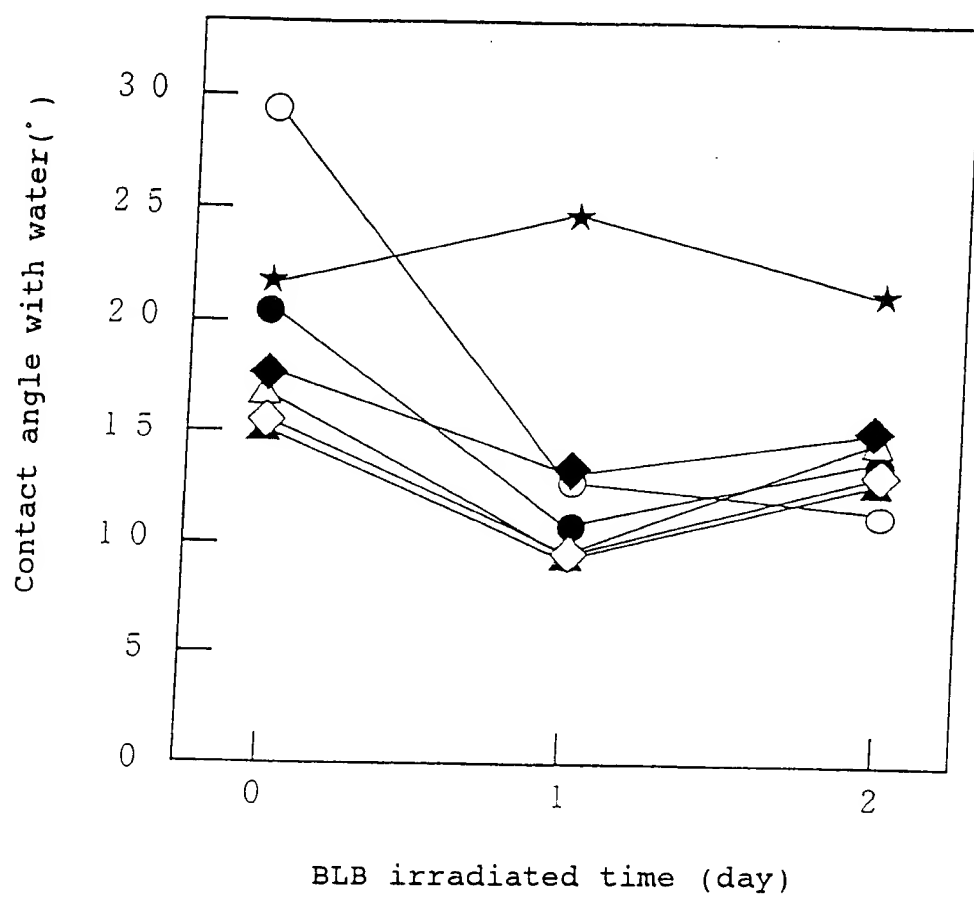
Fig. 1



- ★ 900°C
- 800°C
- 700°C
- △ 600°C
- ▲ 400°C
- ◇ 110°C
- ◆ only glazed tile

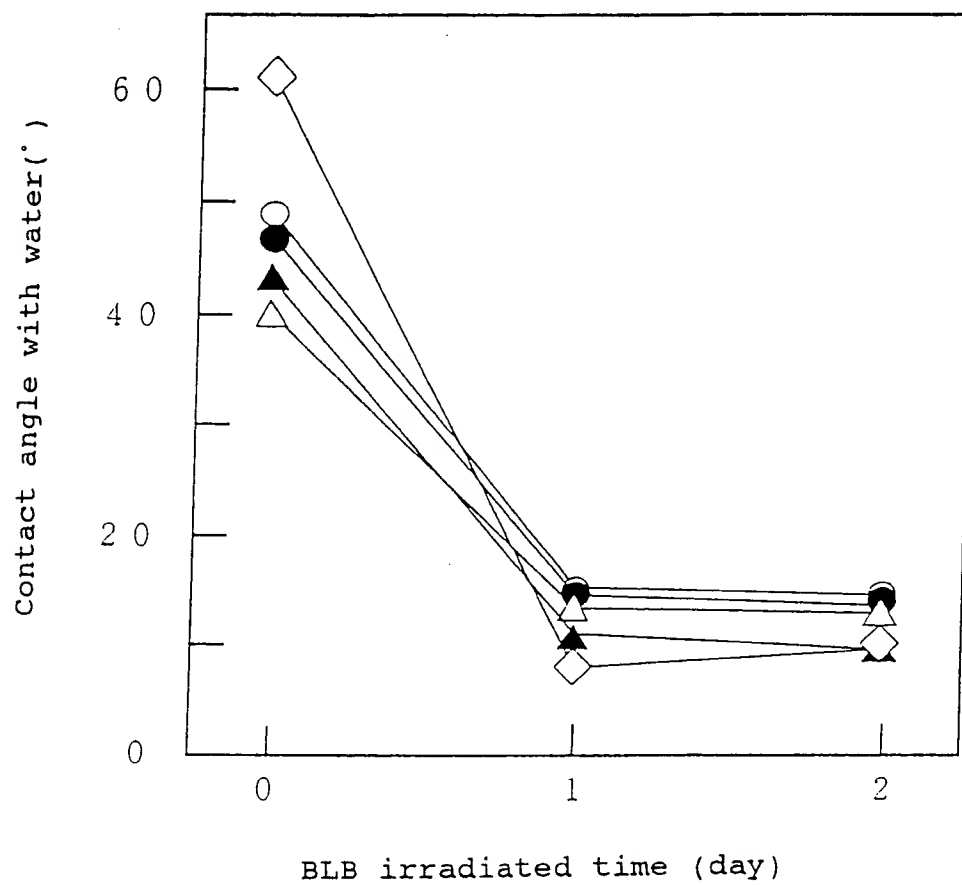
Fig. 2





- ★ 1000°C
- 900°C
- 800°C
- △ 700°C
- ▲ 600°C
- ◇ 400°C
- ◆ 110°C

Fig. 3



- 800°C
- 700°C
- △ 600°C
- ▲ 400°C
- ◇ 110°C

Fig. 4

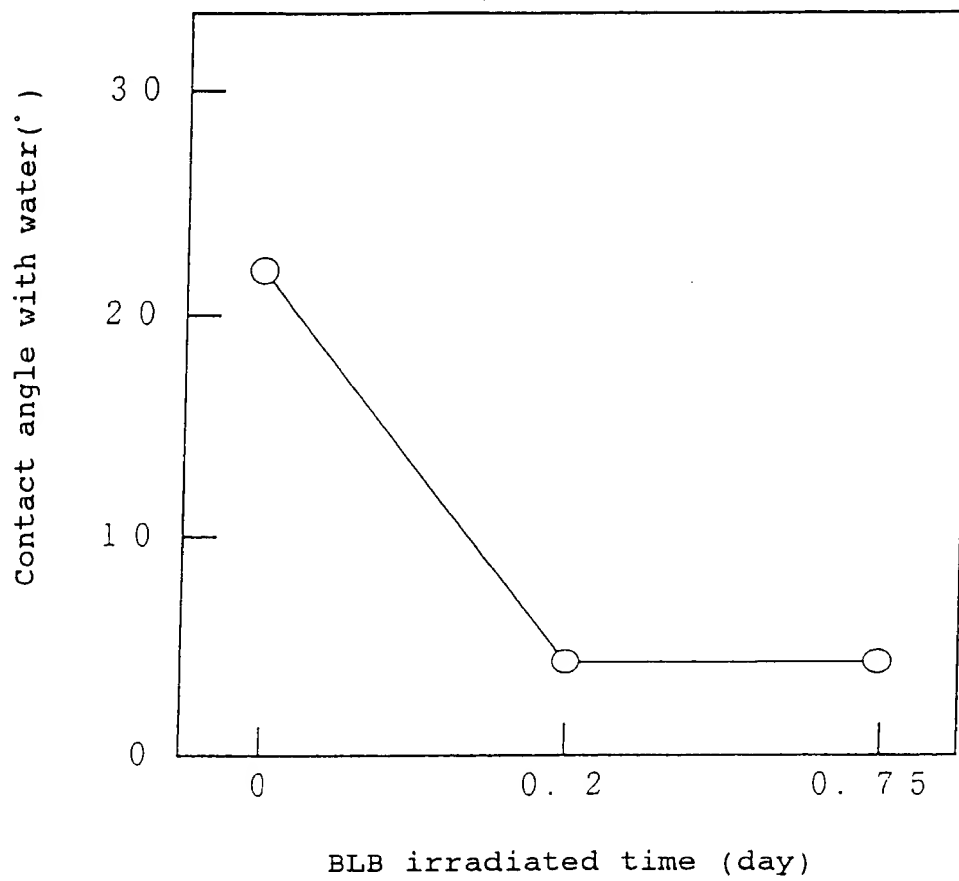


Fig. 5

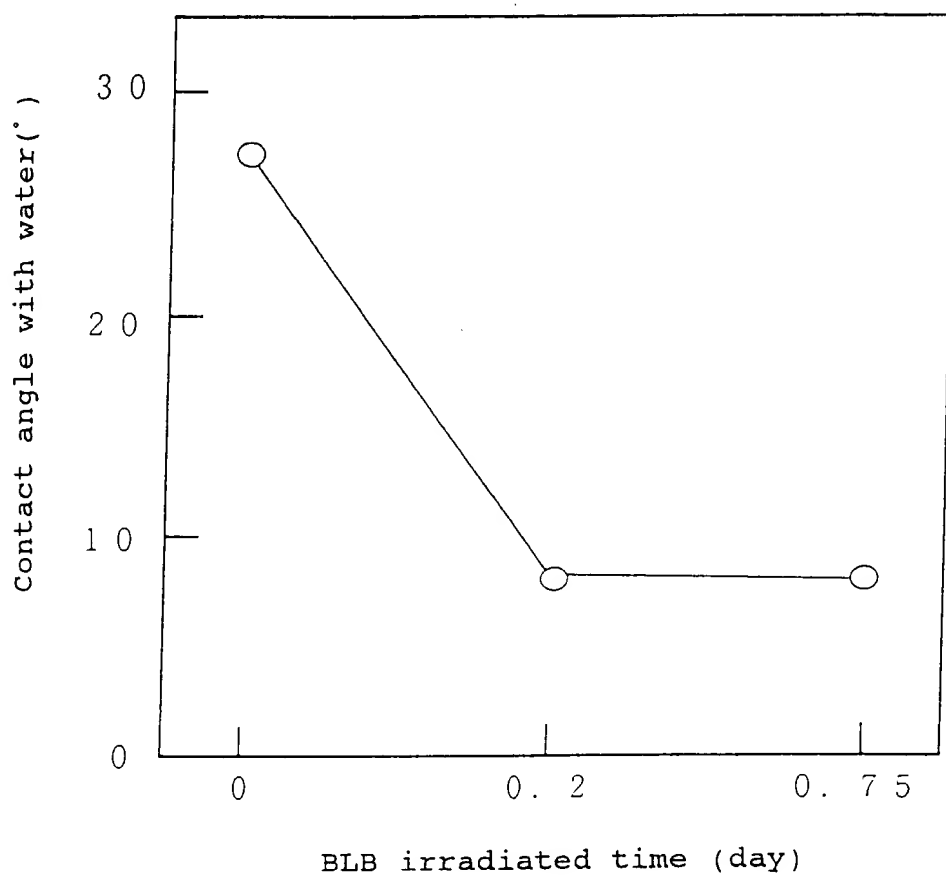


Fig. 6

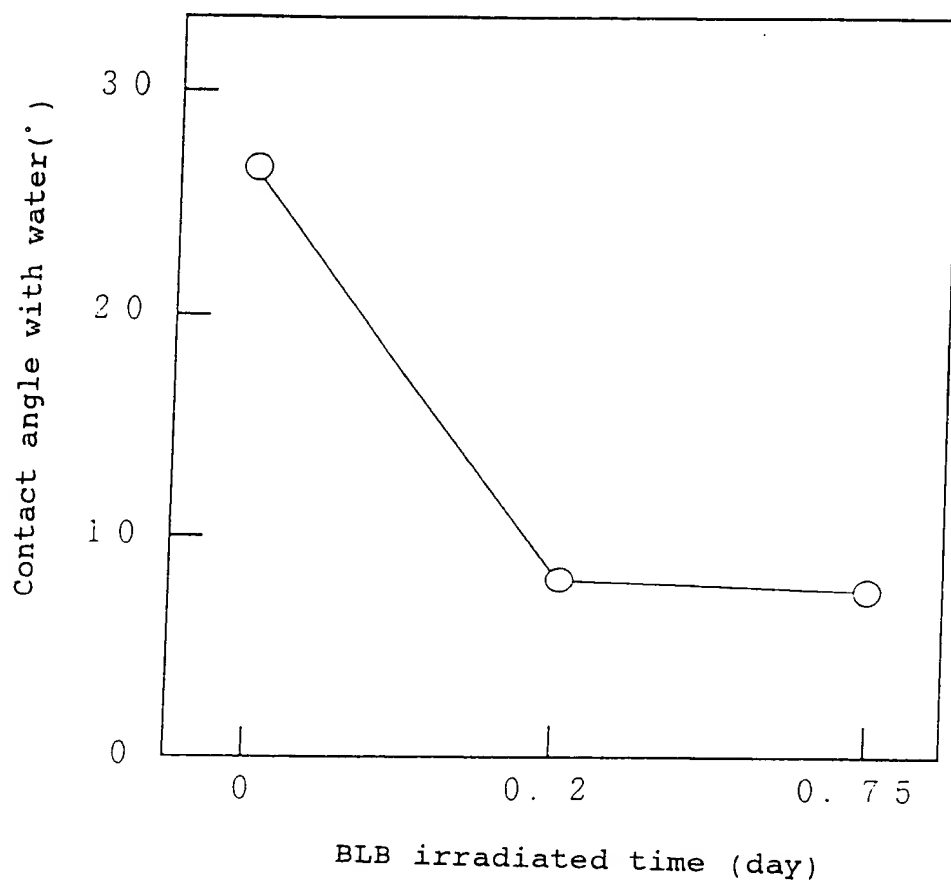


Fig. 7

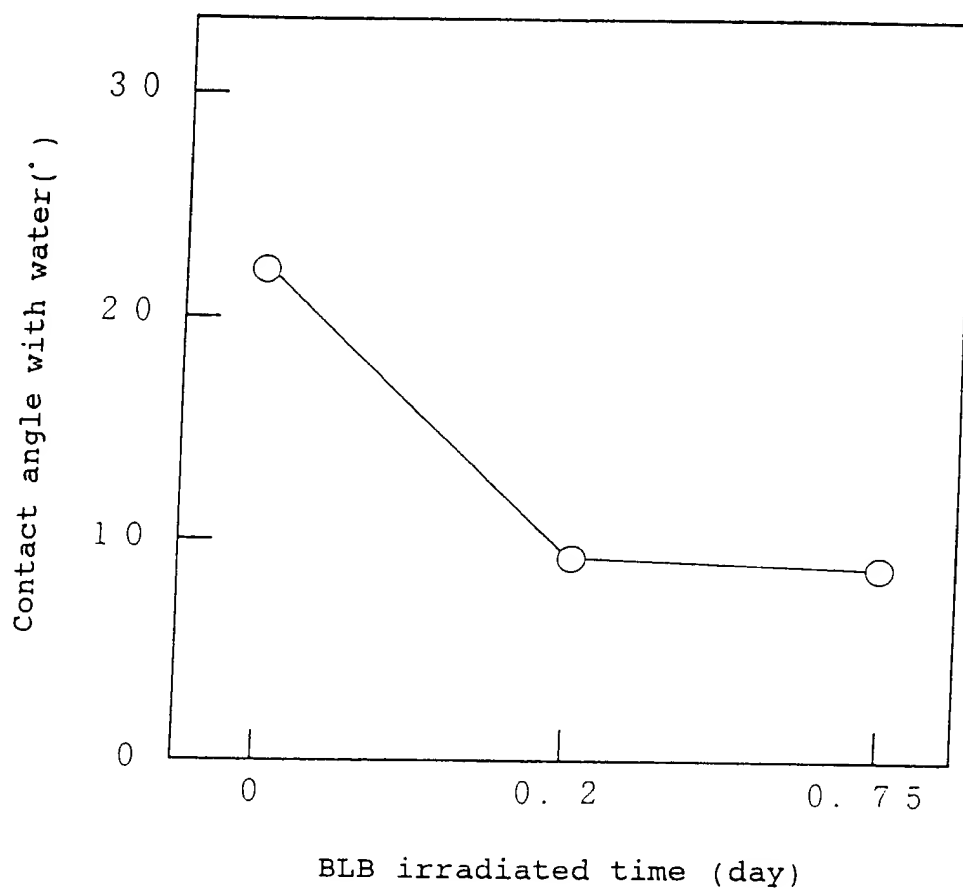


Fig. 8

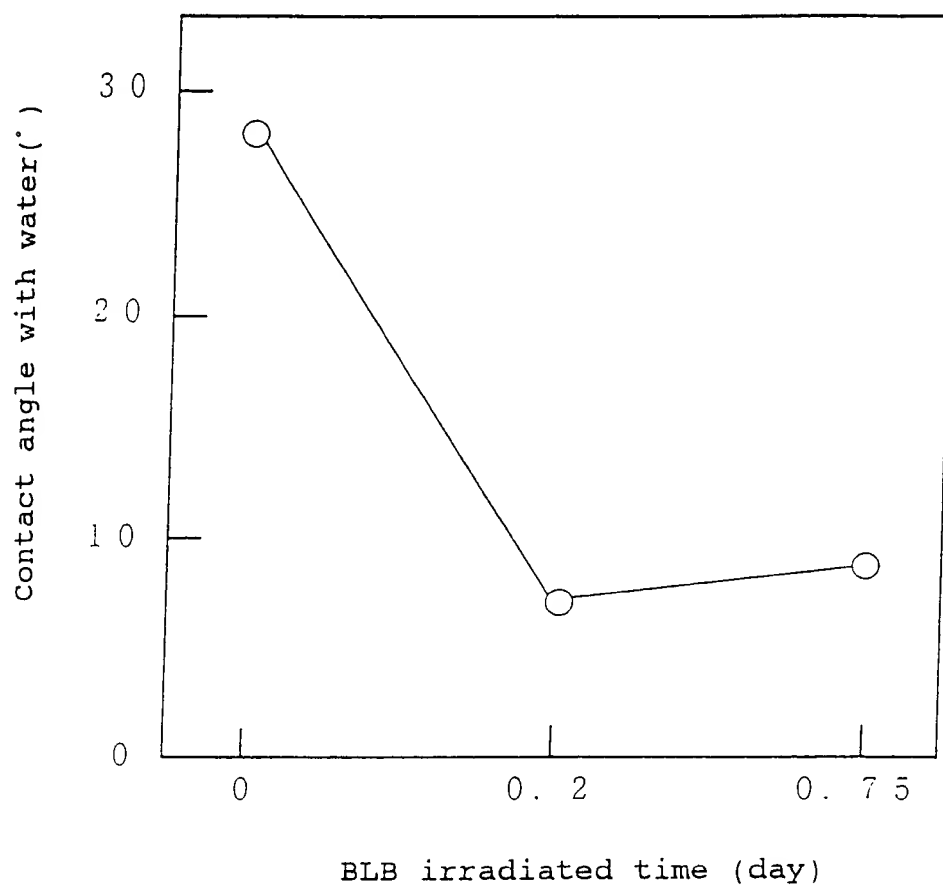


Fig. 9

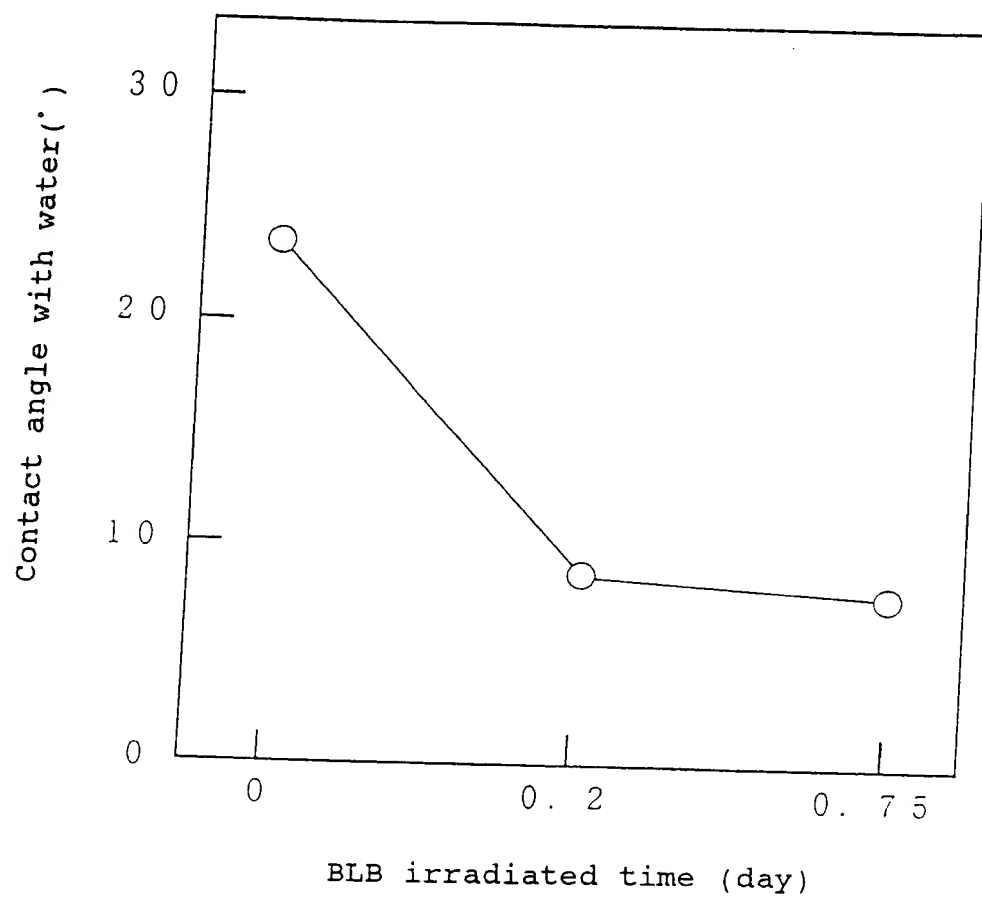


Fig. 10



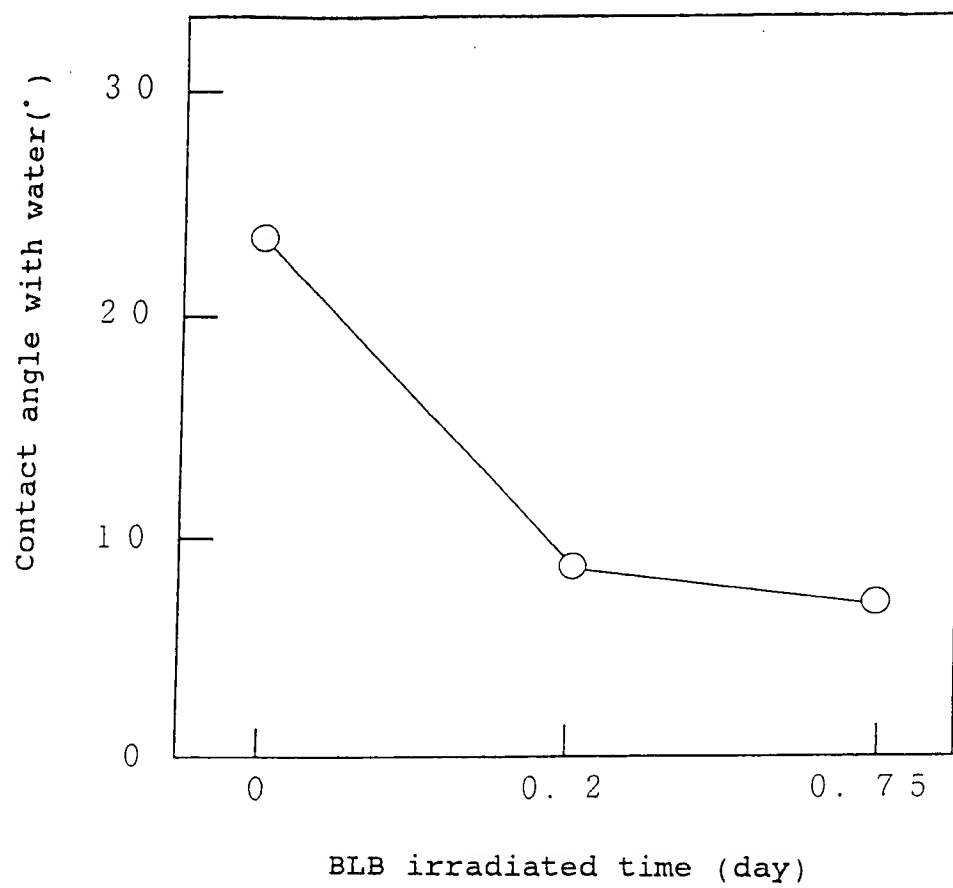


Fig. 11

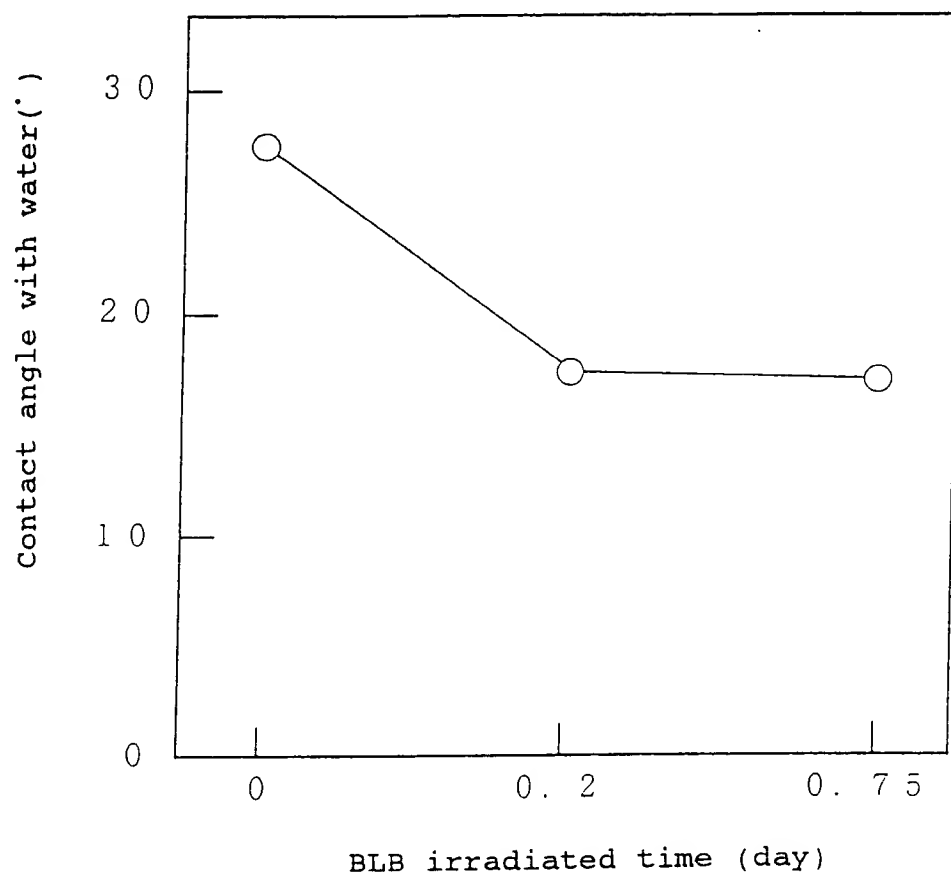


Fig. 12

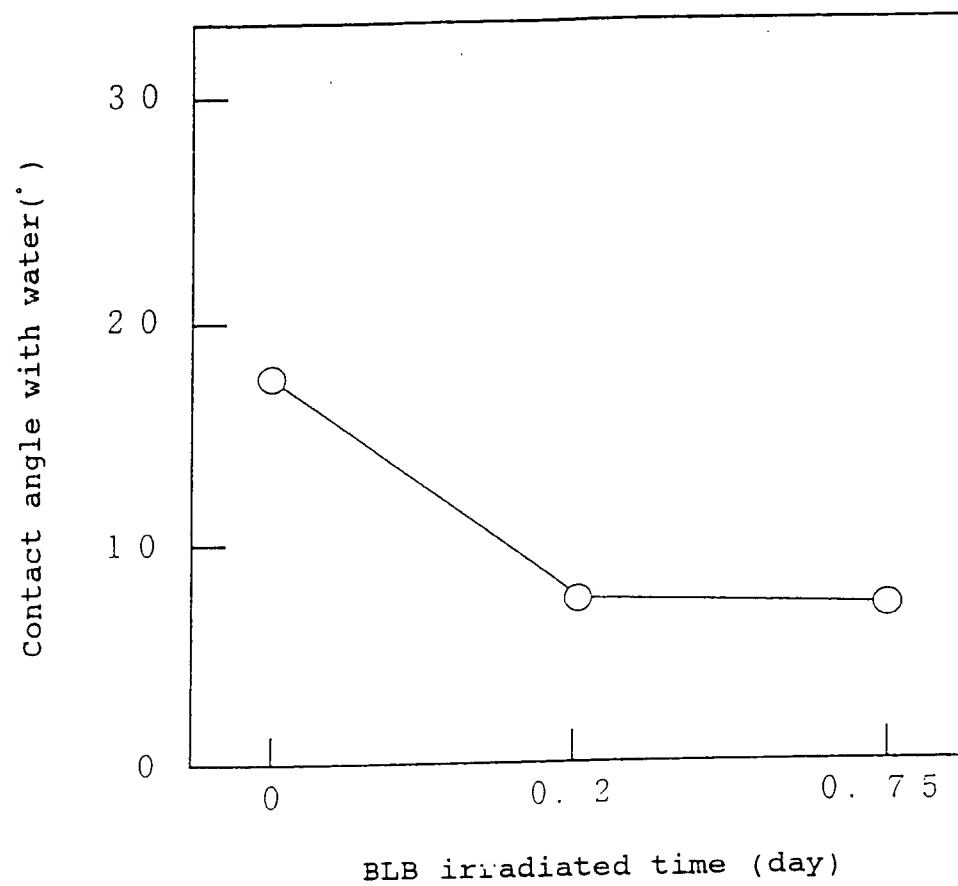


Fig. 13

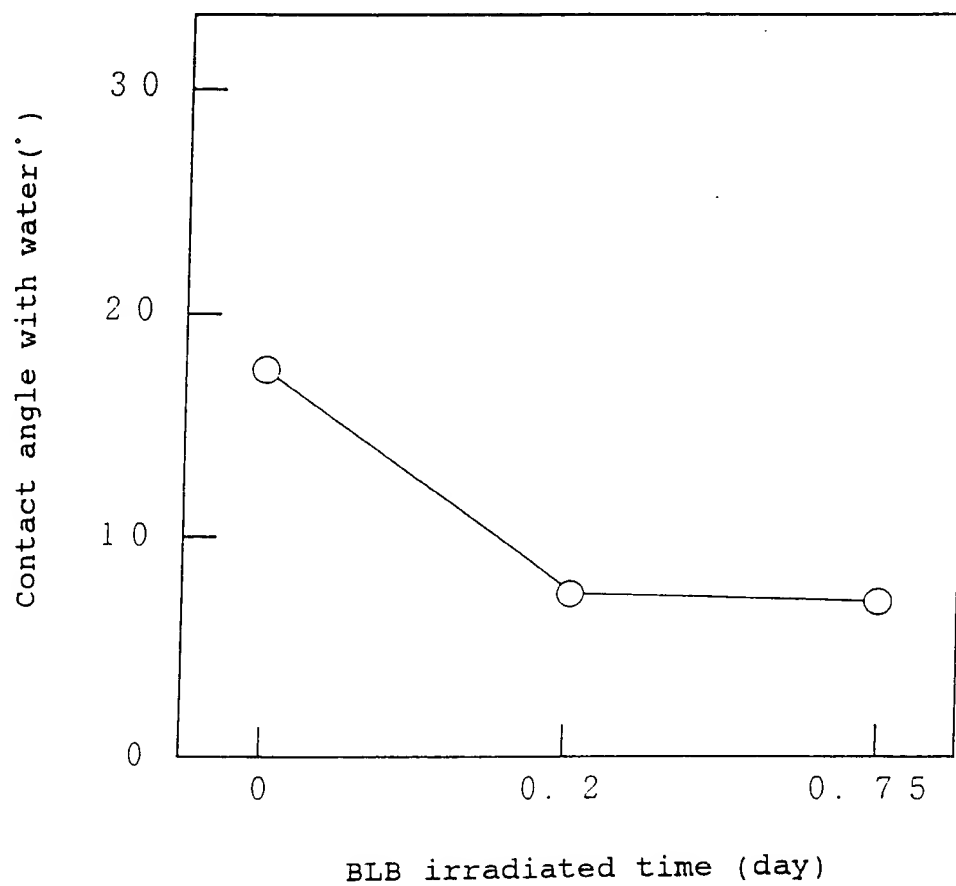


Fig. 14

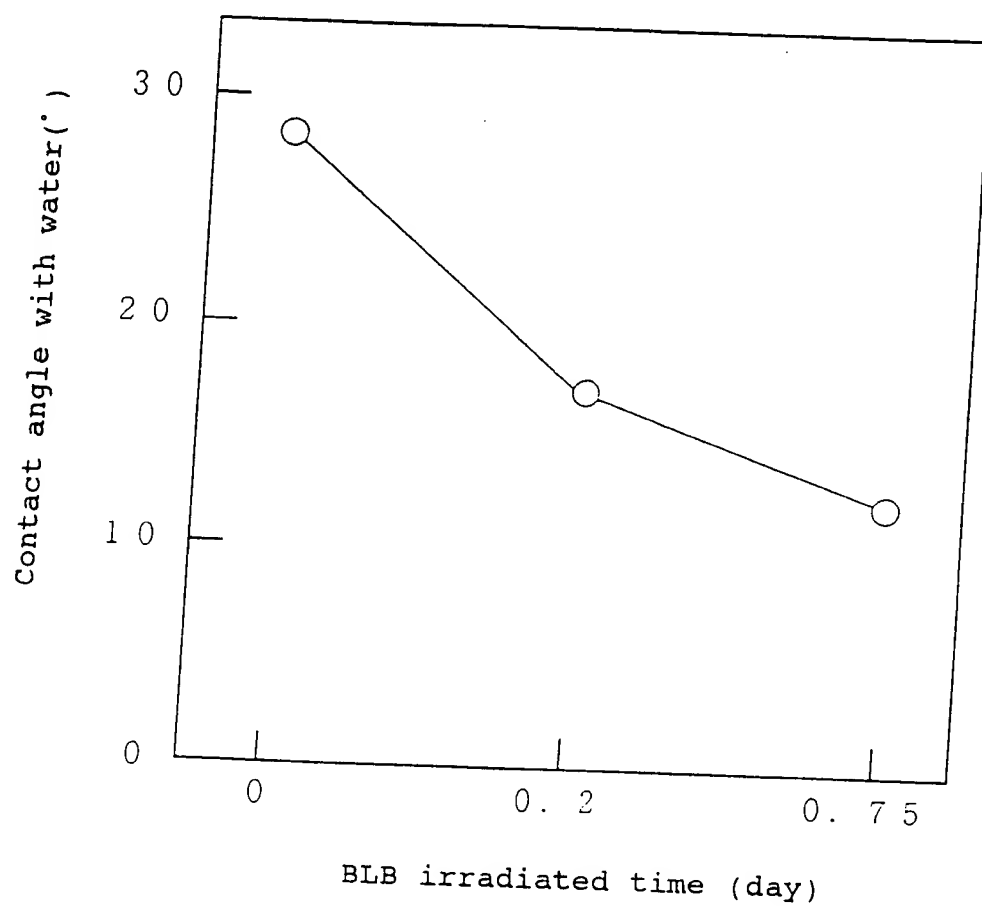


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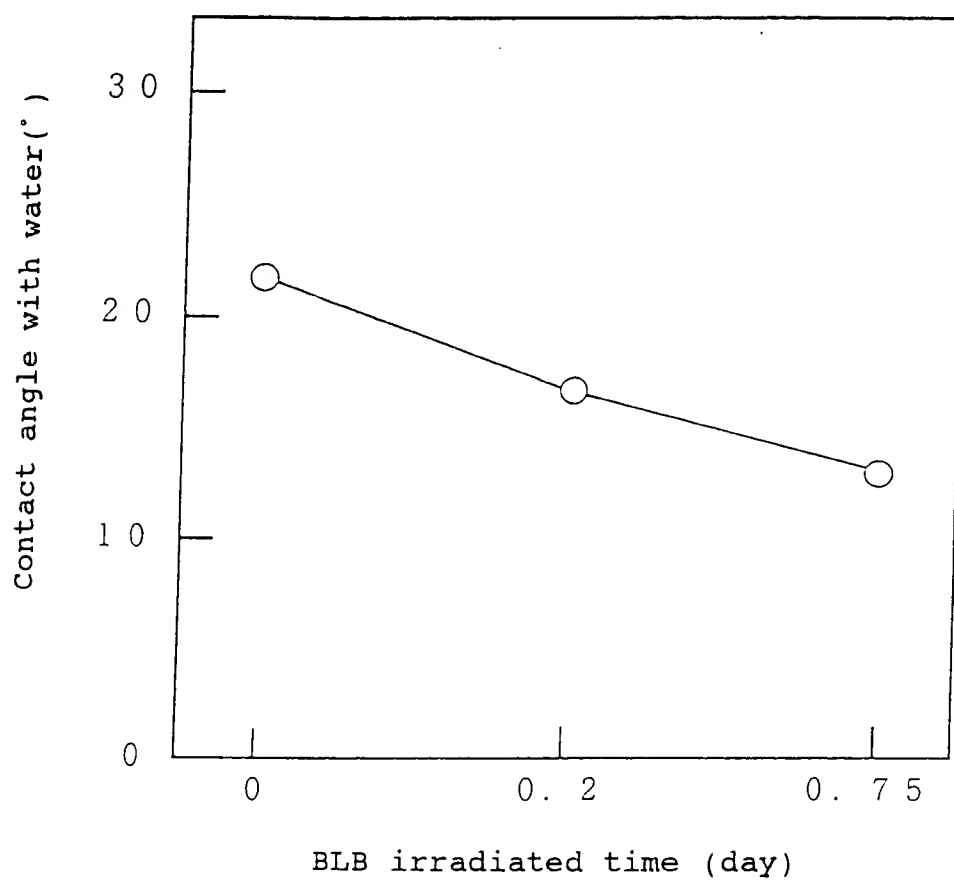


Fig. 16

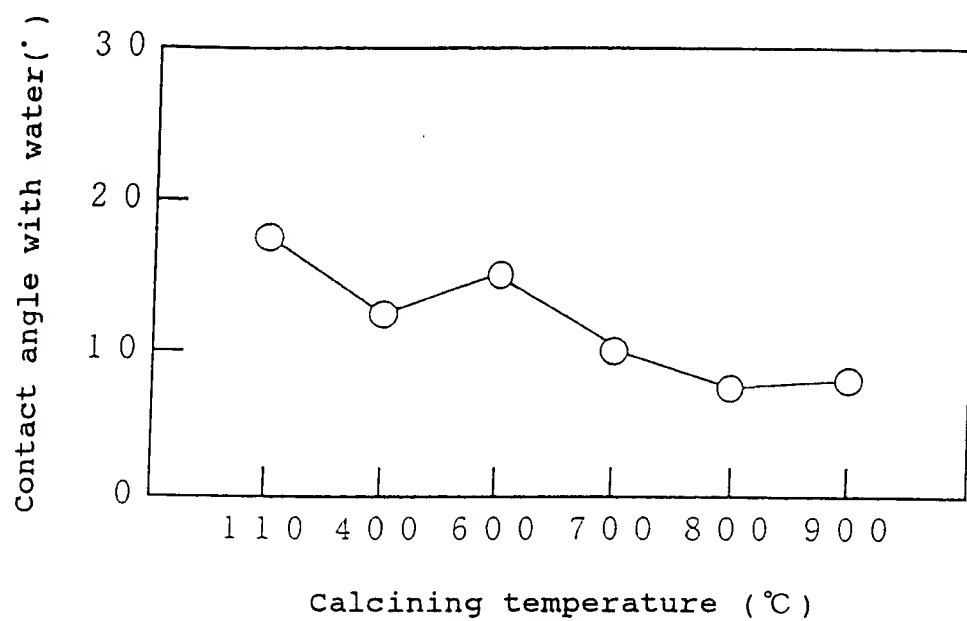


Fig. 17

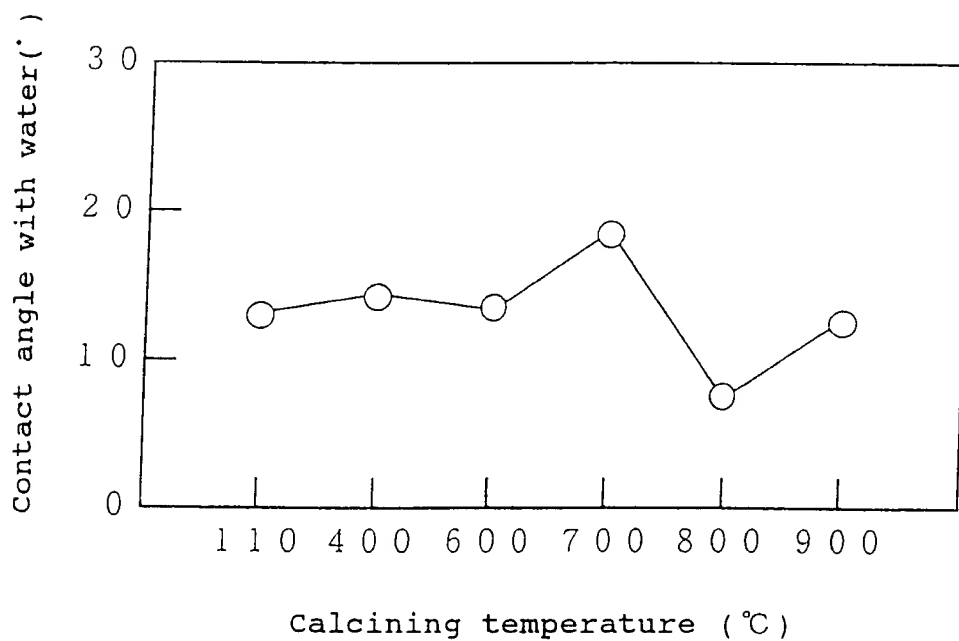


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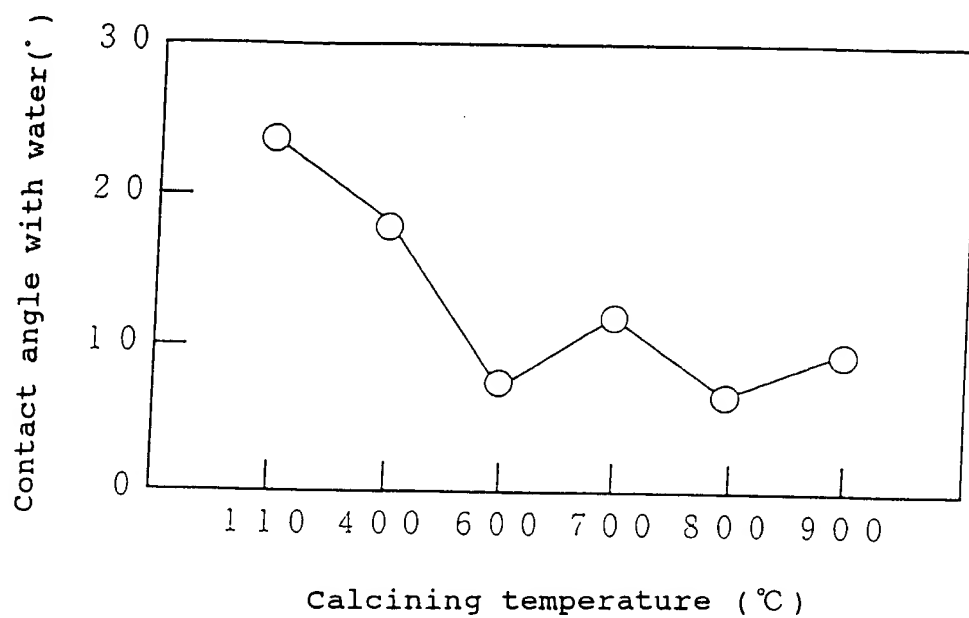


Fig. 19

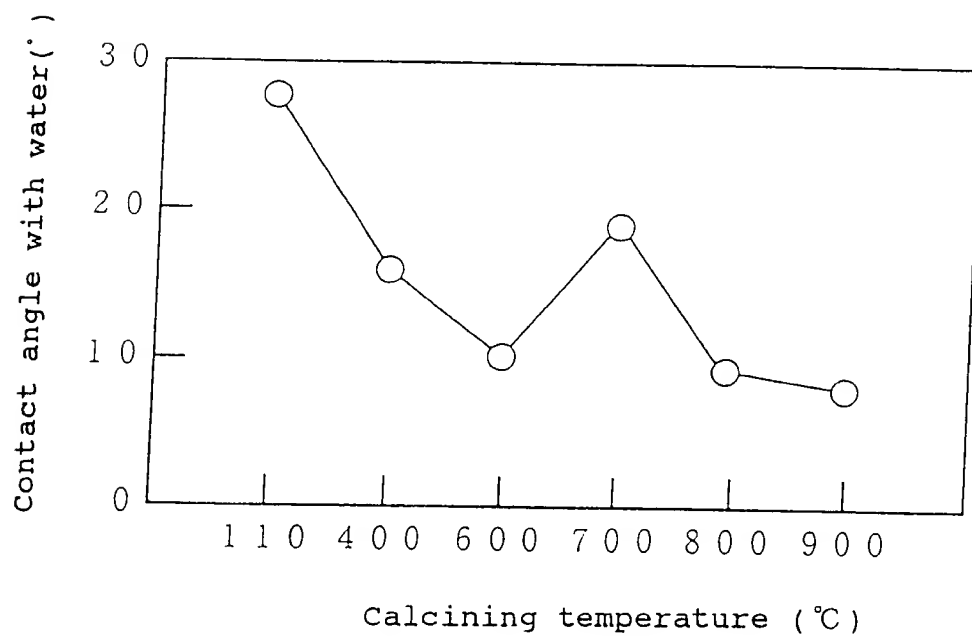


Fig. 20



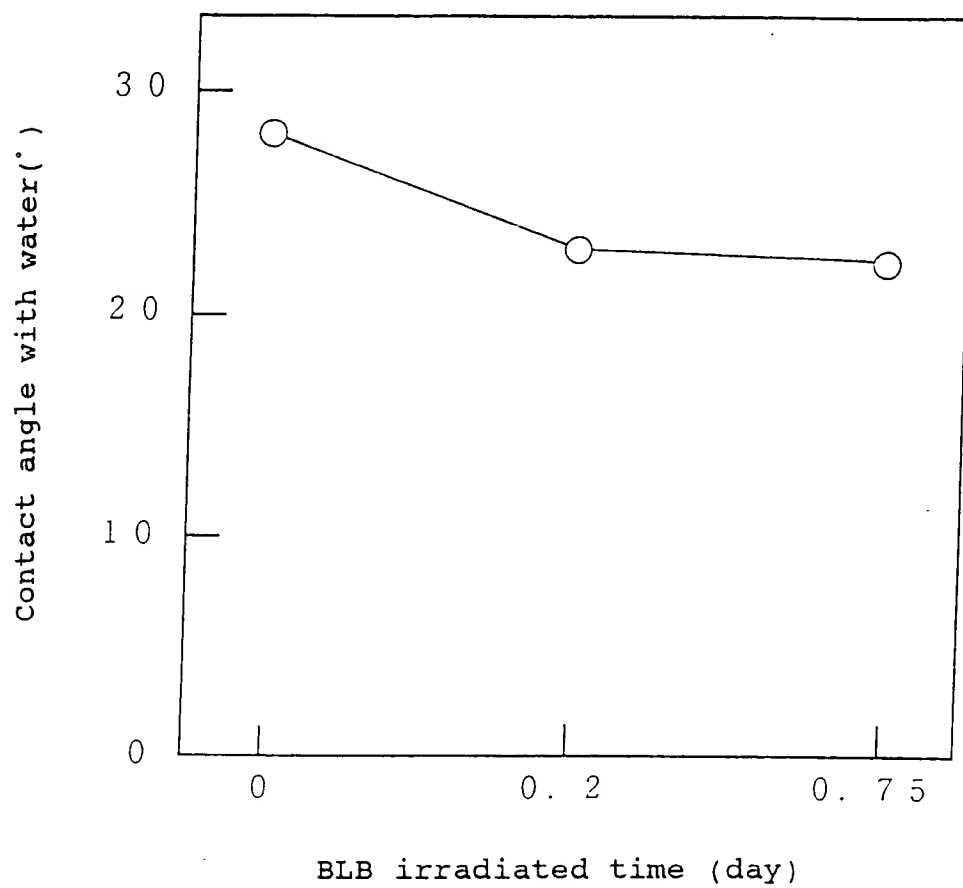


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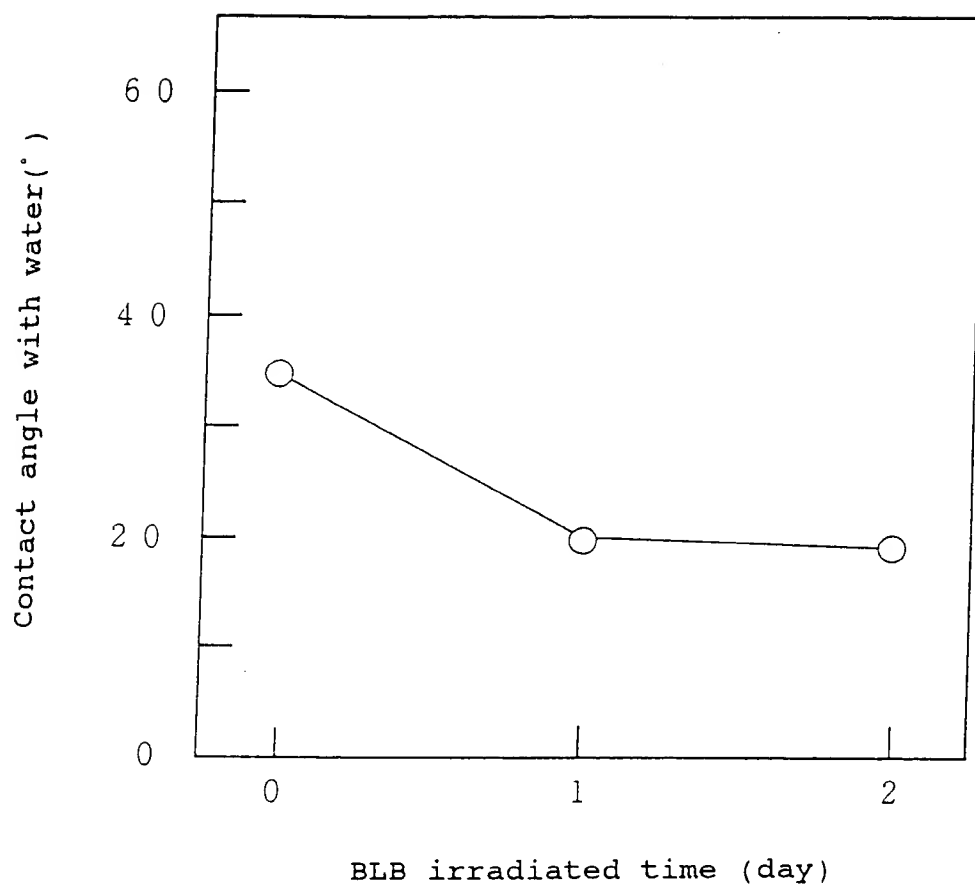


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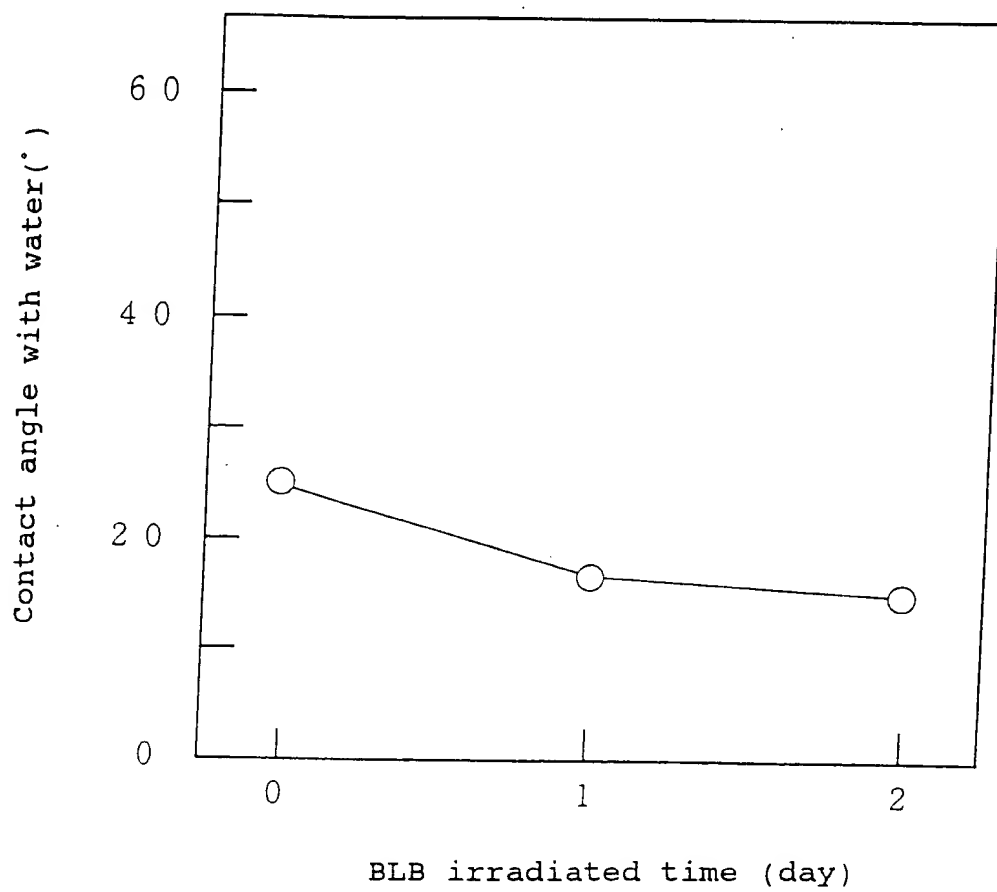


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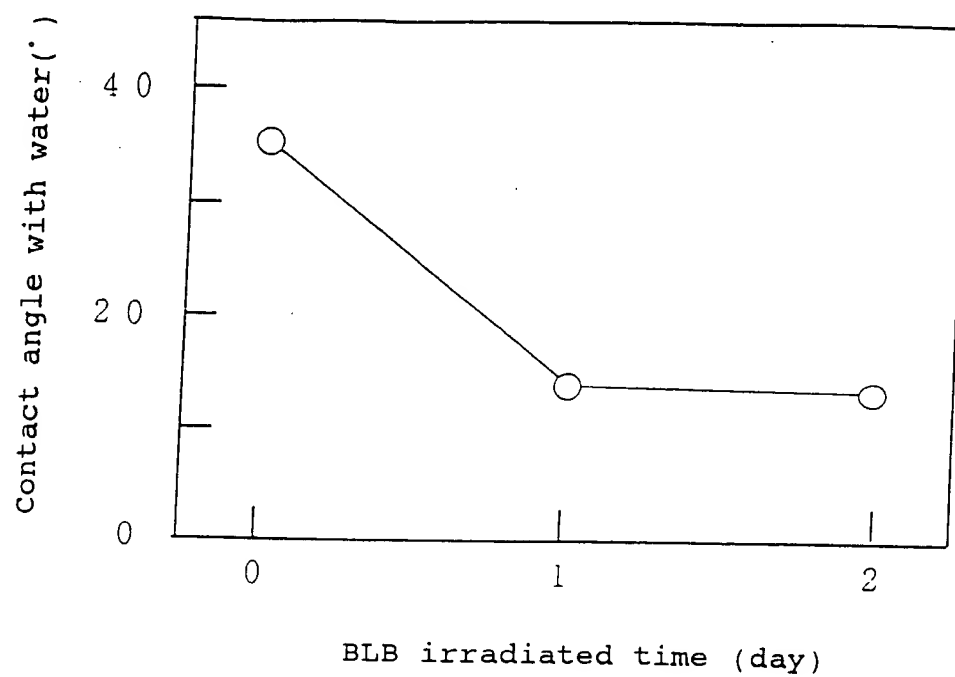


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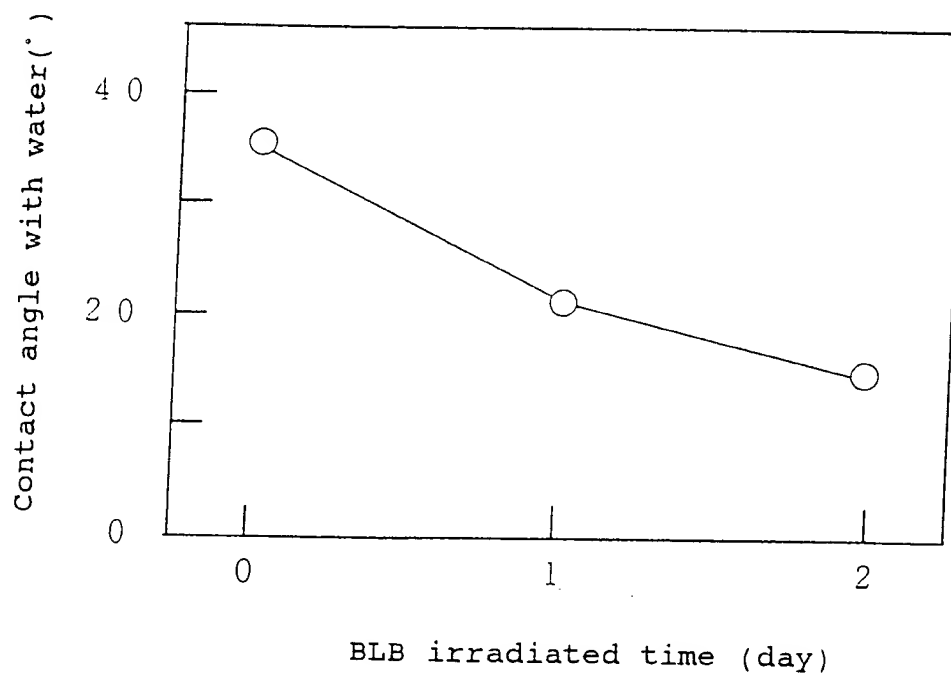


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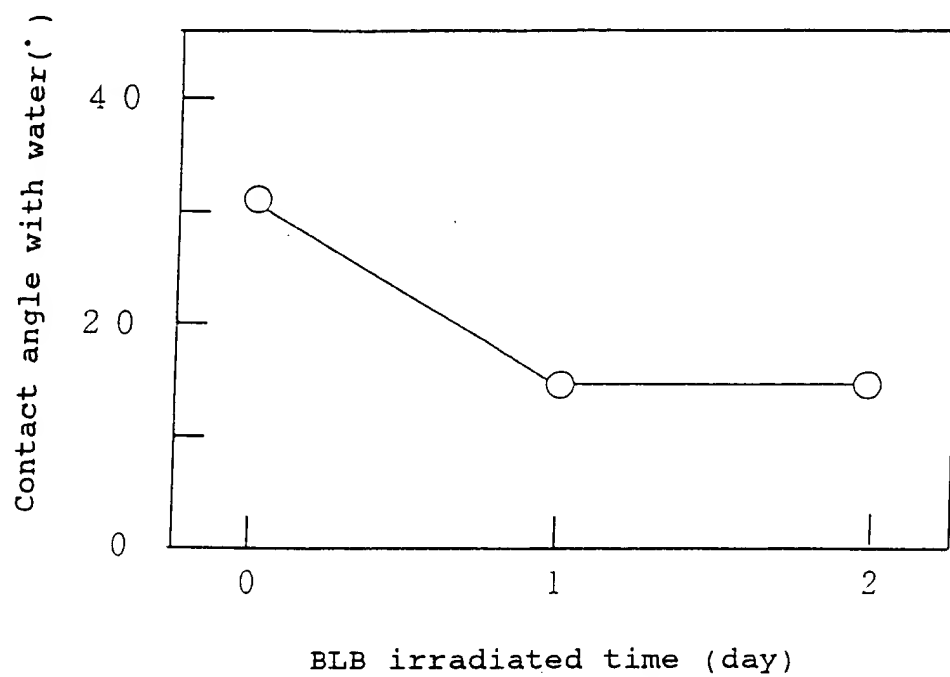


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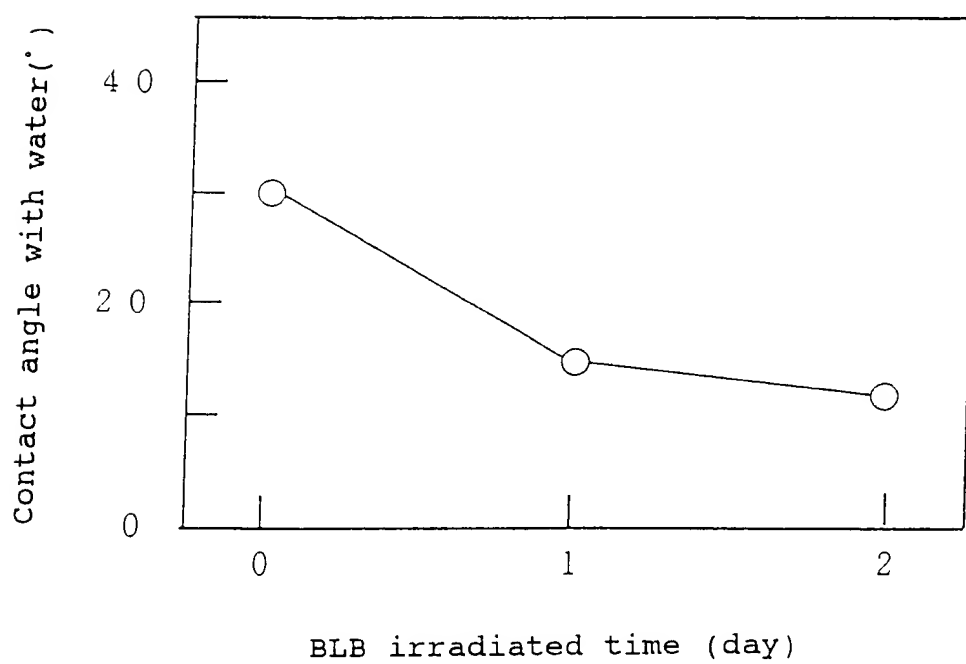


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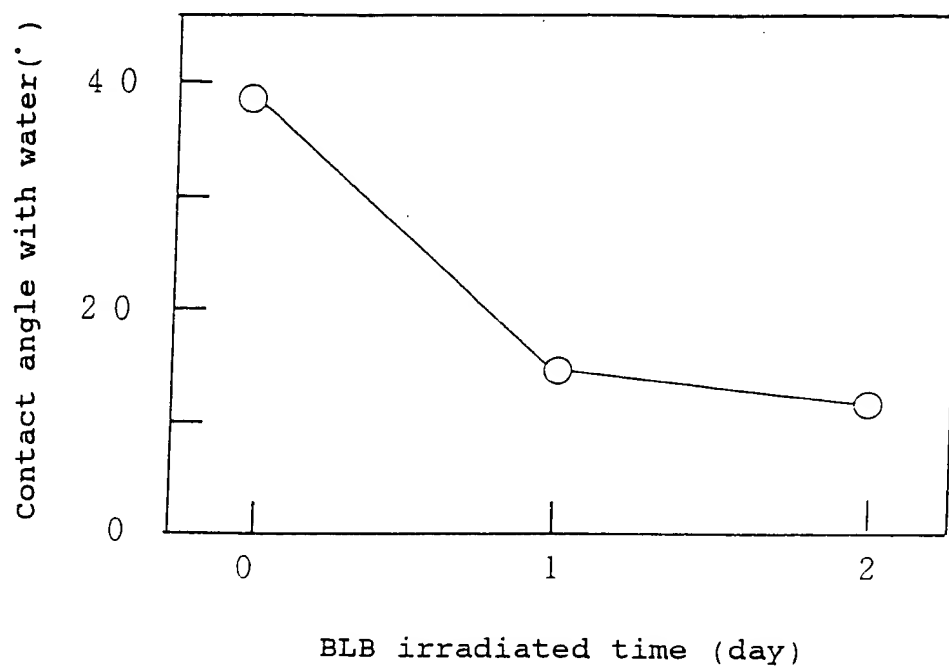


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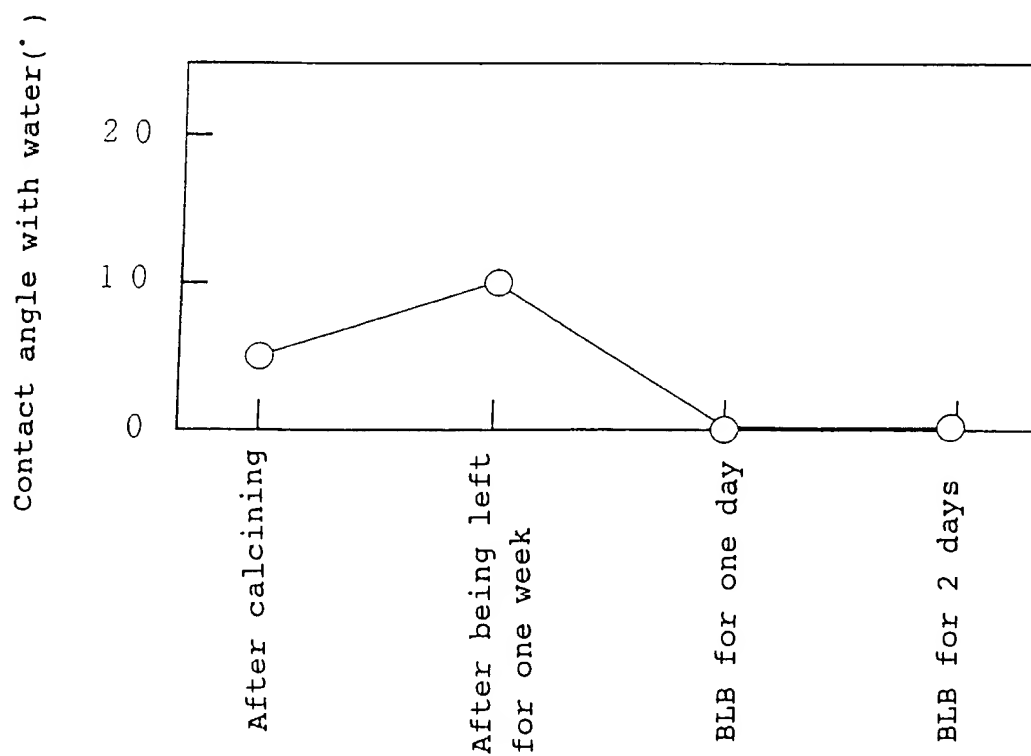


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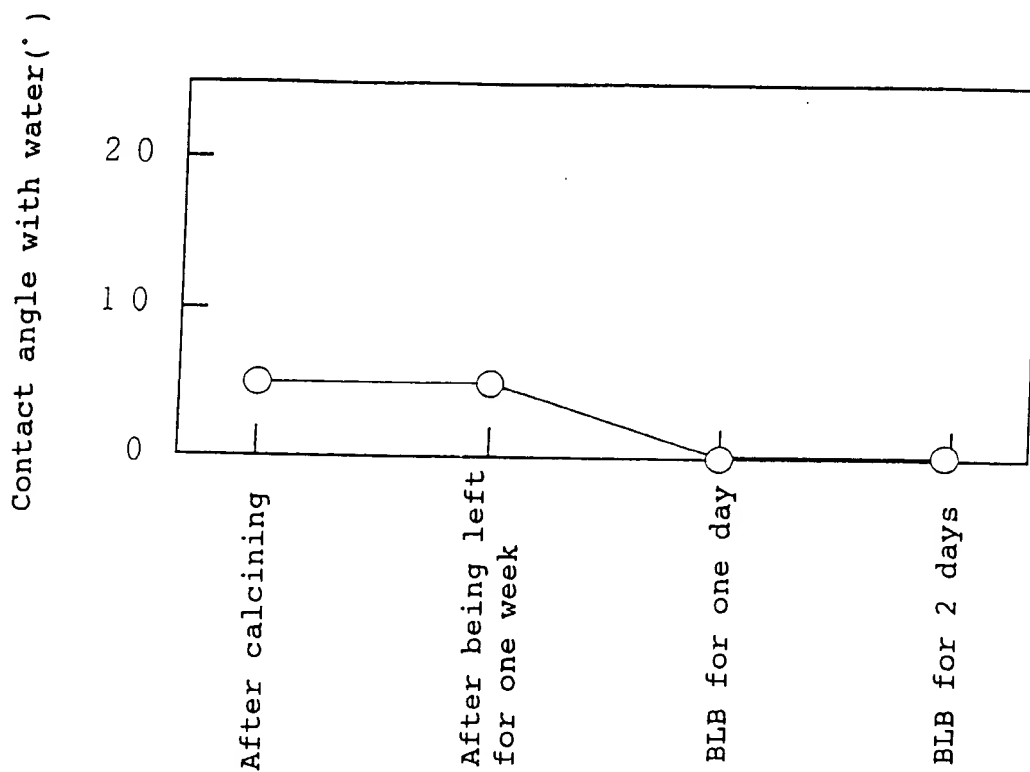


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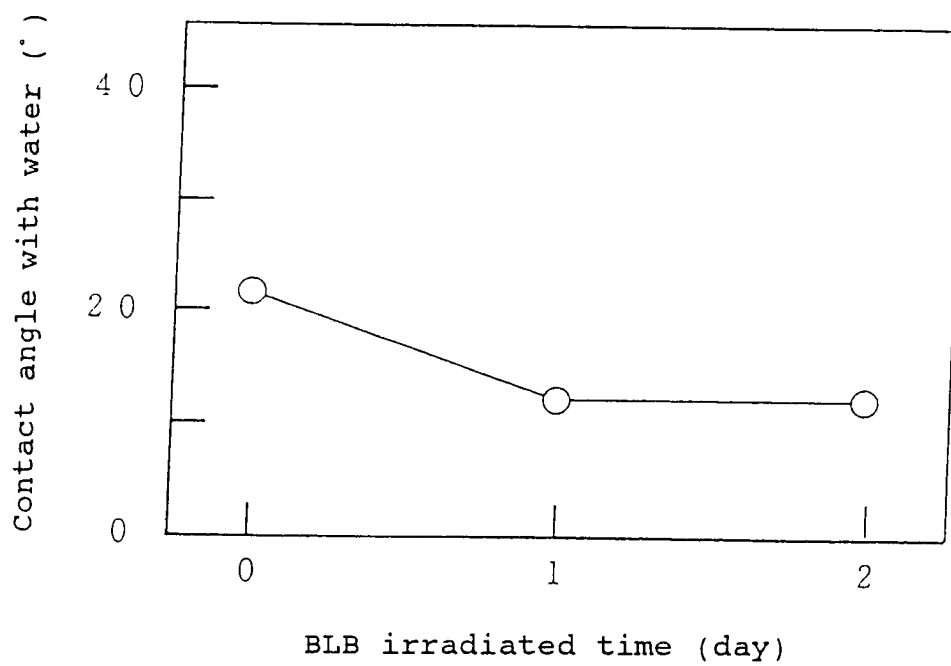


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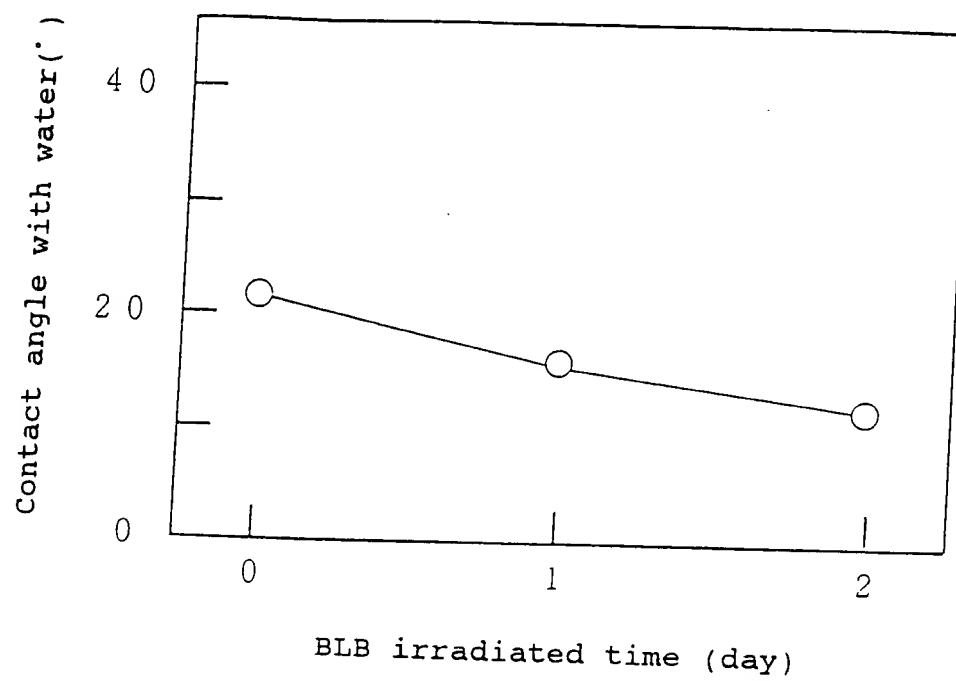


Fig. 32

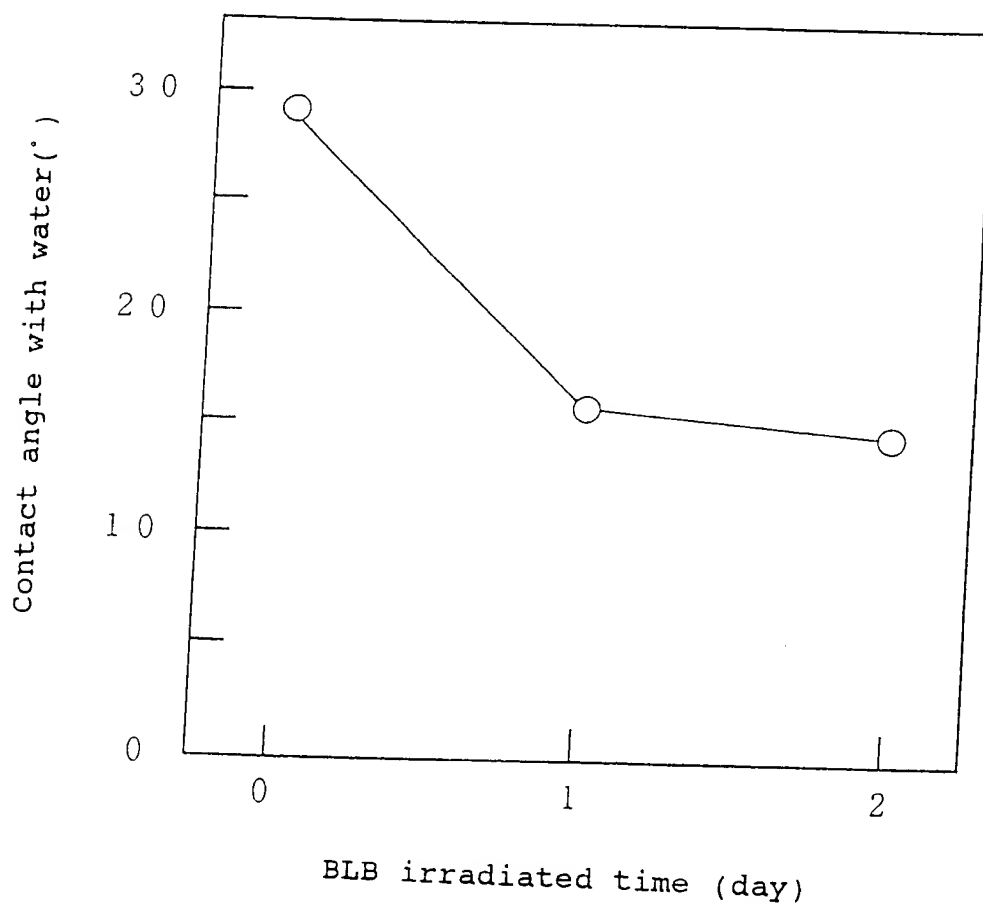


Fig. 33



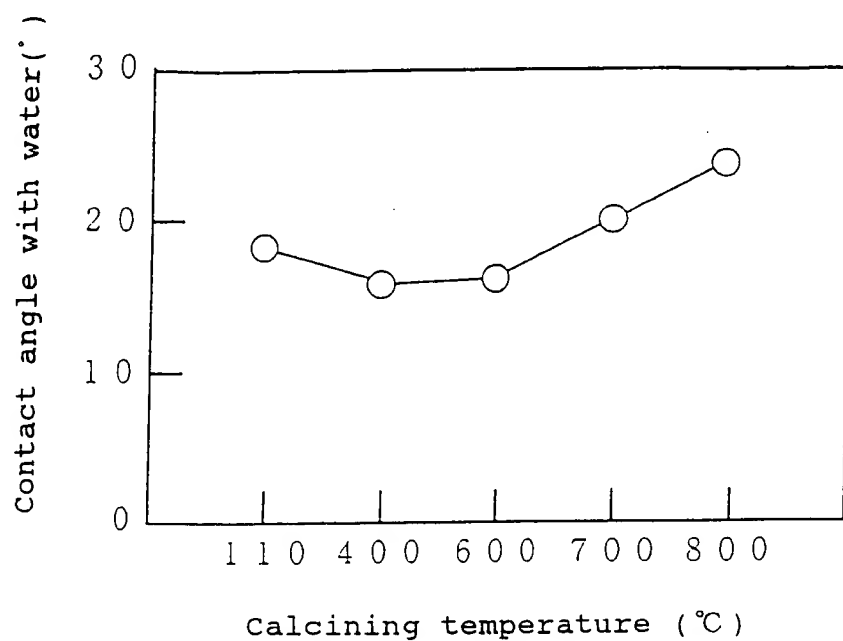
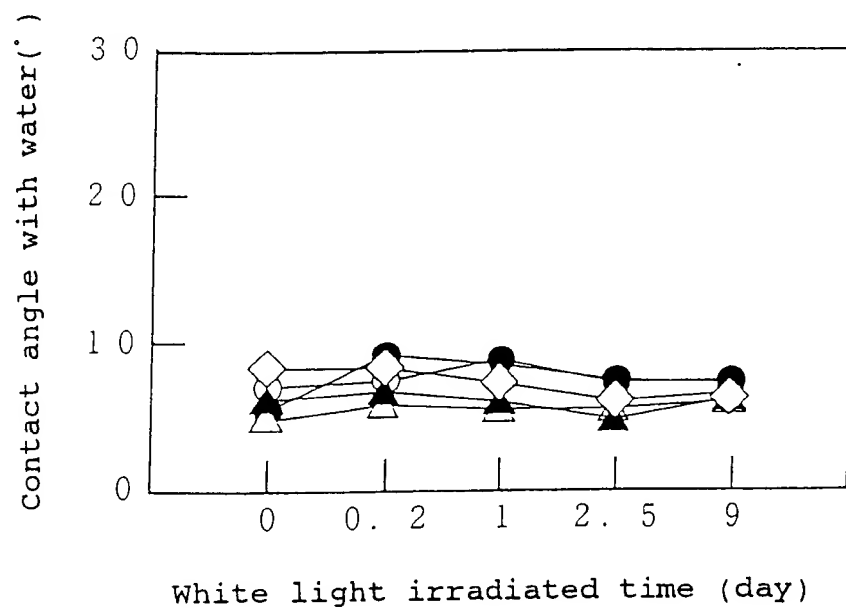


Fig. 34



- 800°C
- 700°C
- △ 600°C
- ▲ 400°C
- ◇ 110°C

Fig. 35

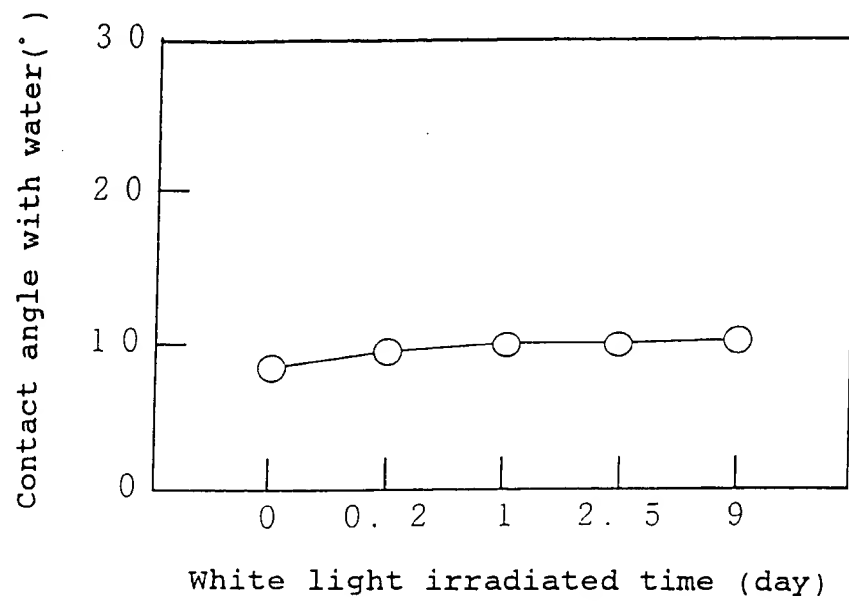


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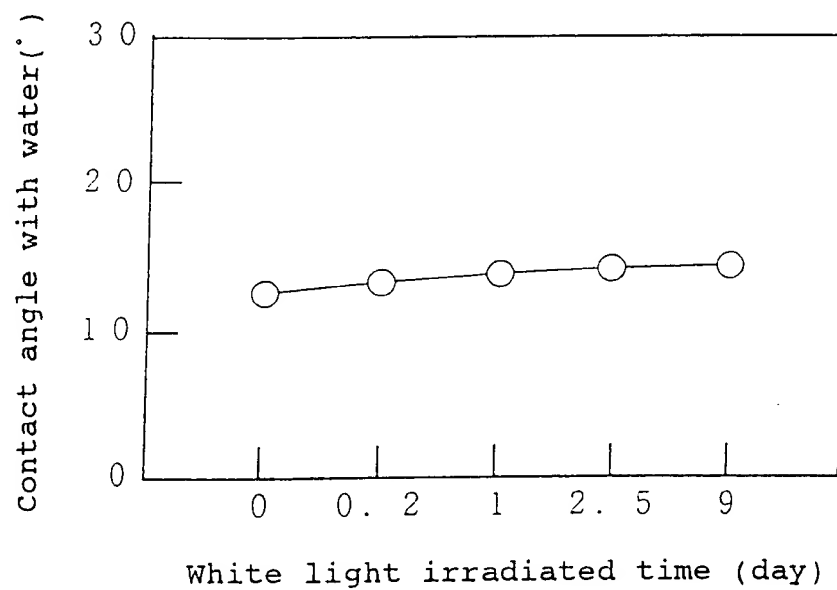


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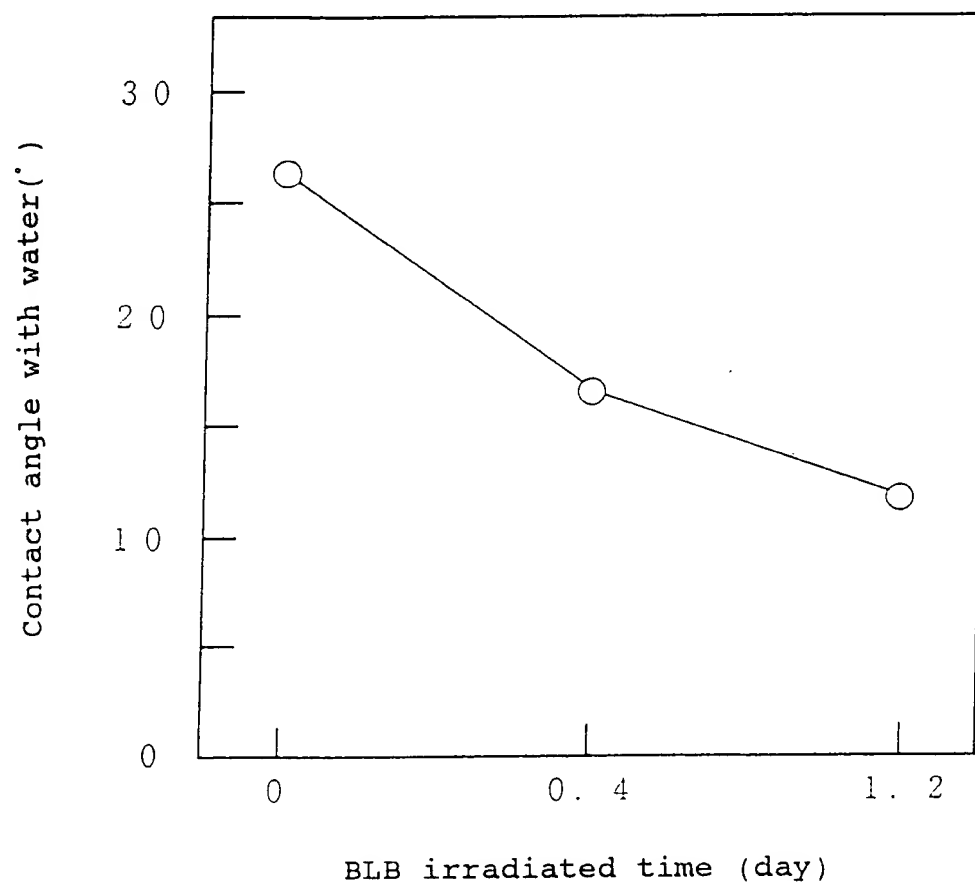


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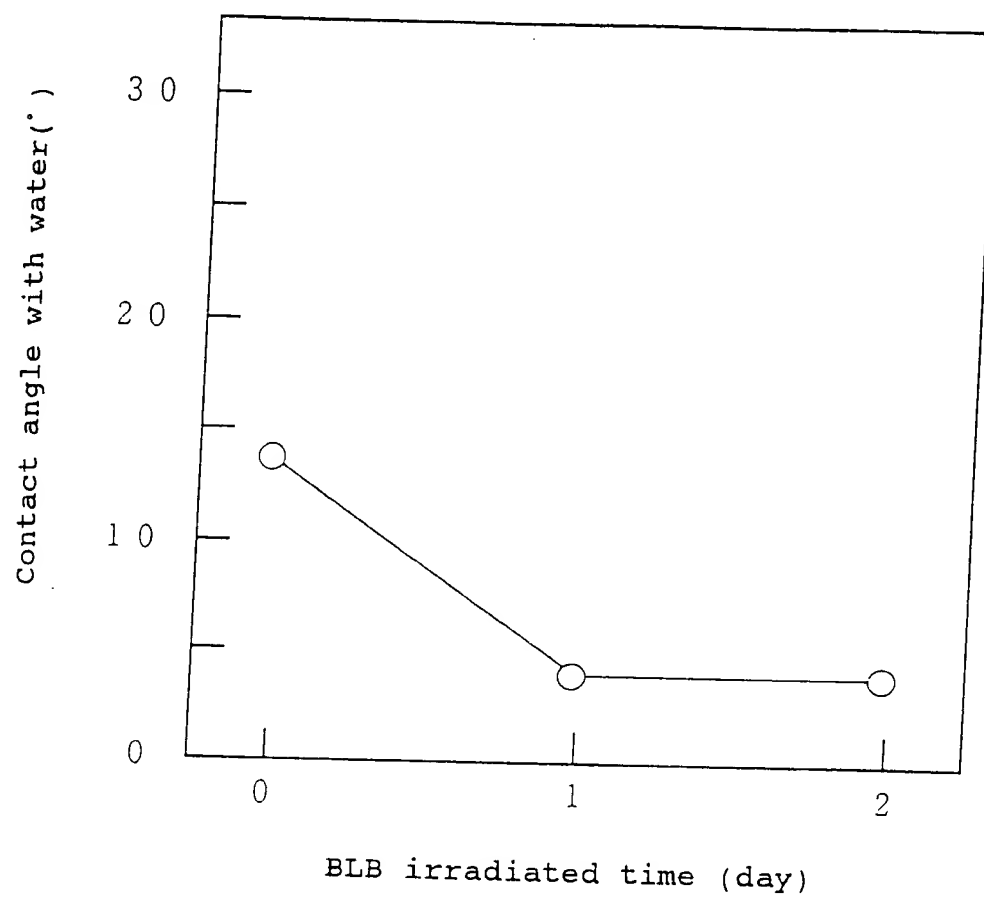


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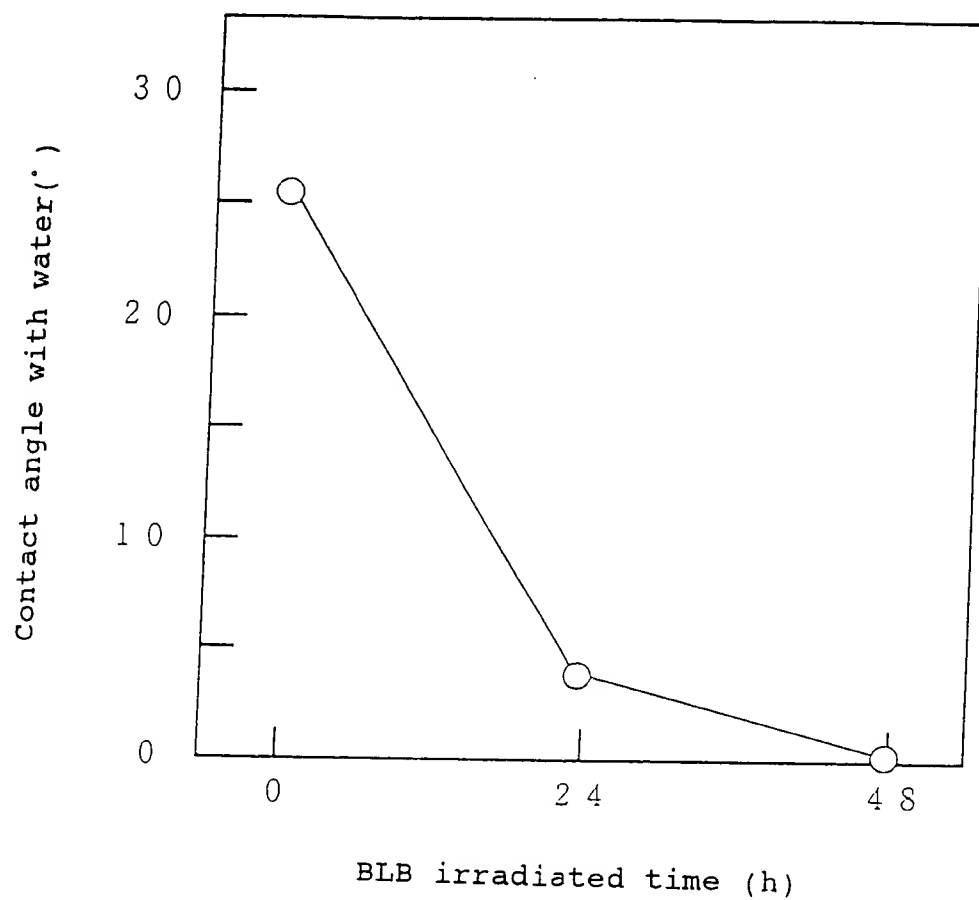


Fig. 40

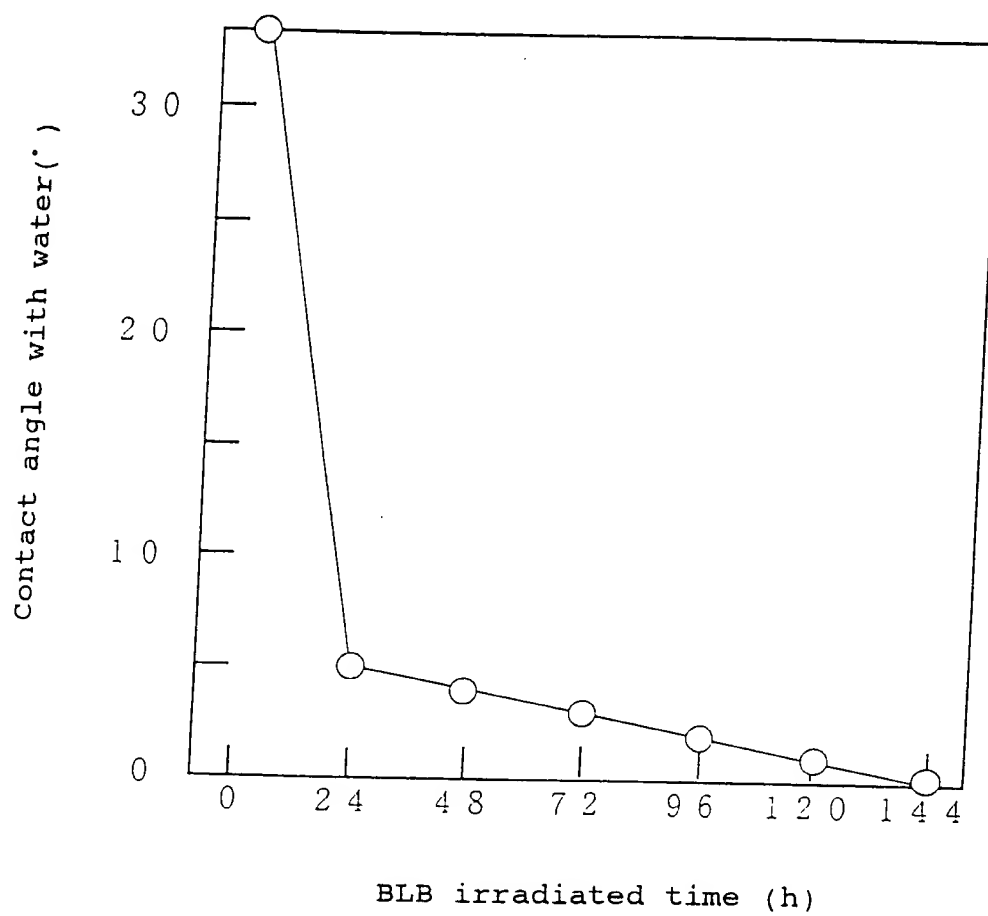


Fig. 41

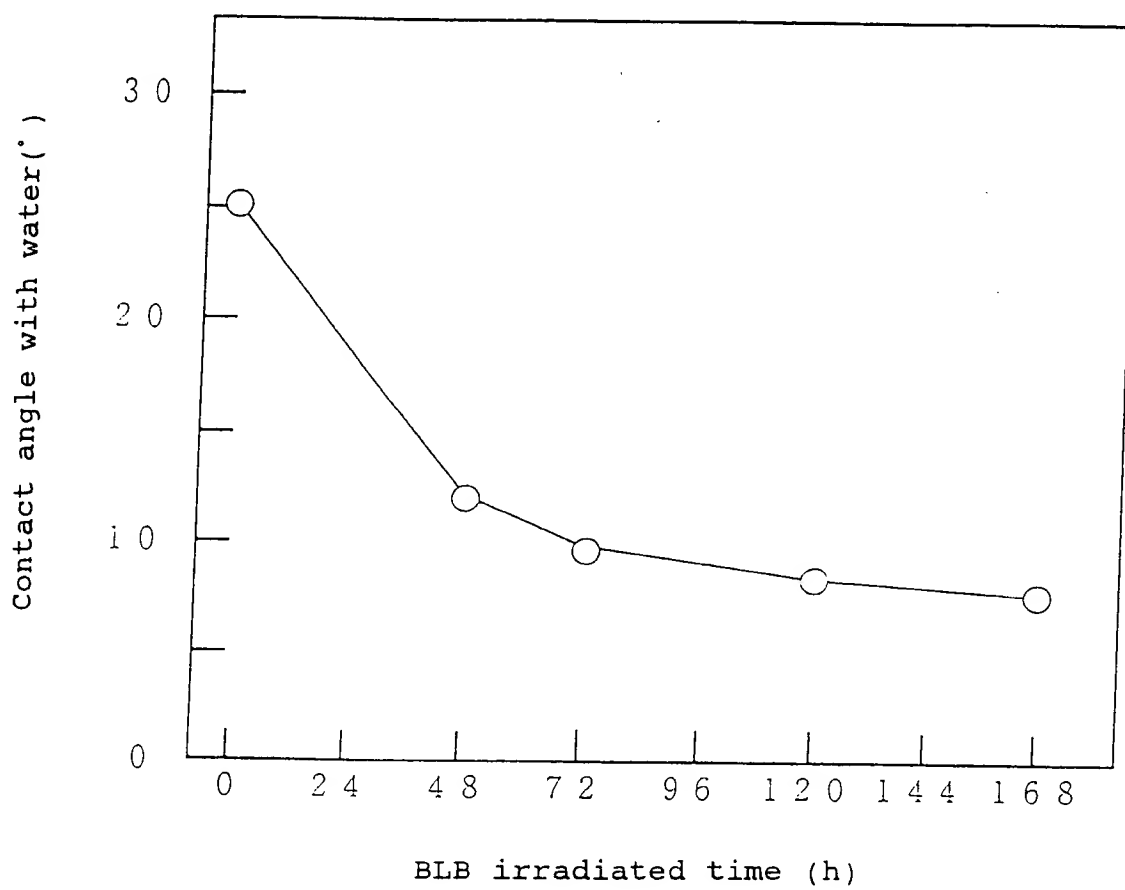


Fig. 42

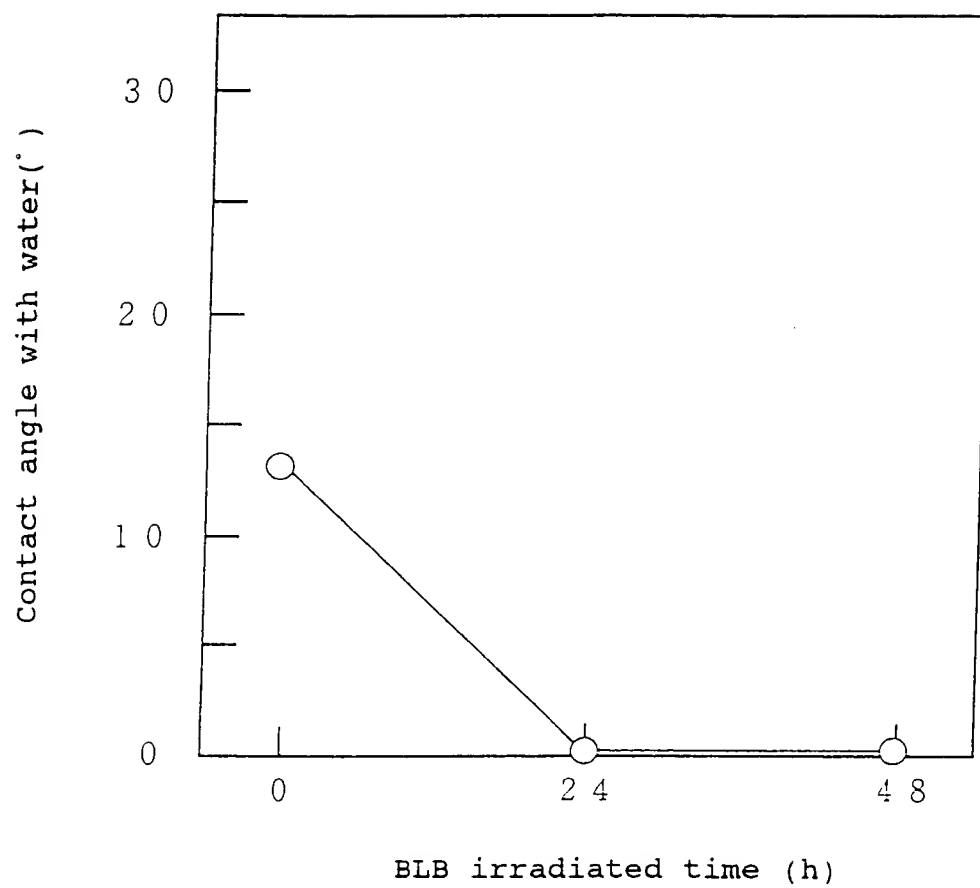


Fig. 43



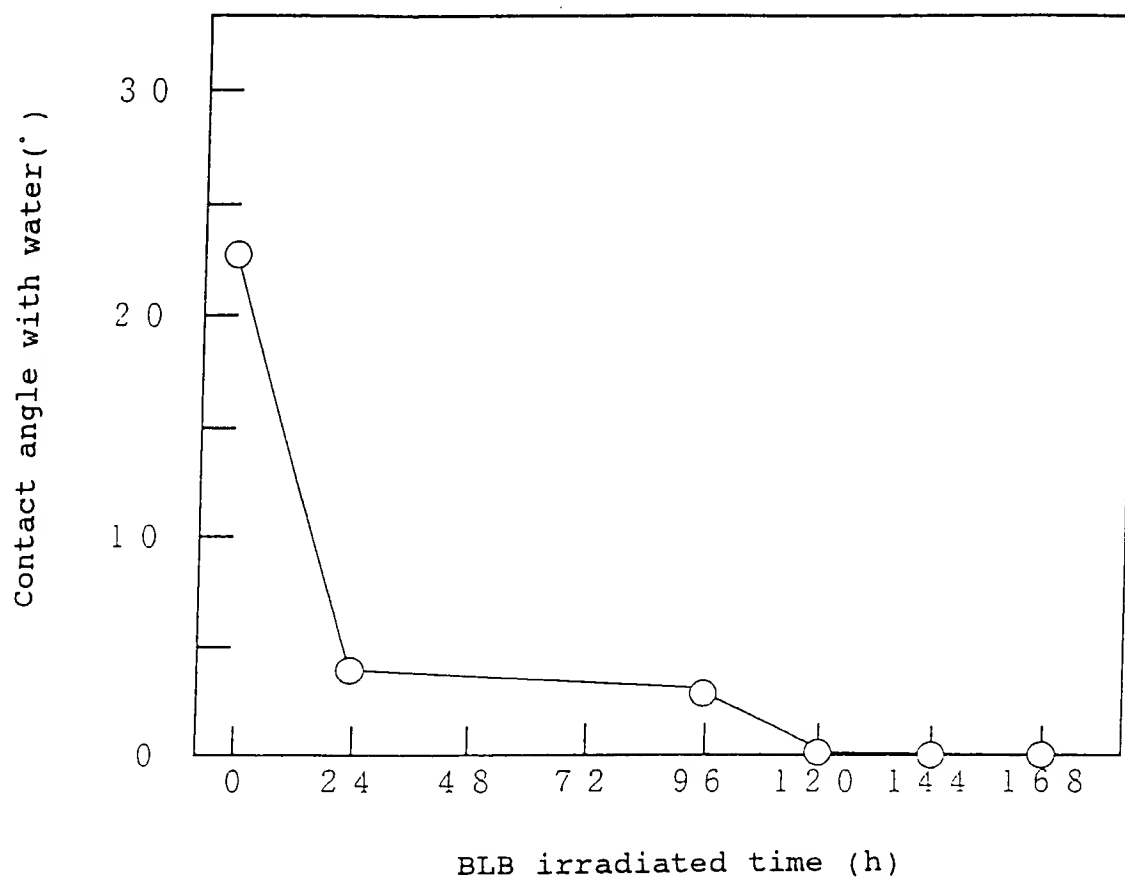


Fig. 44

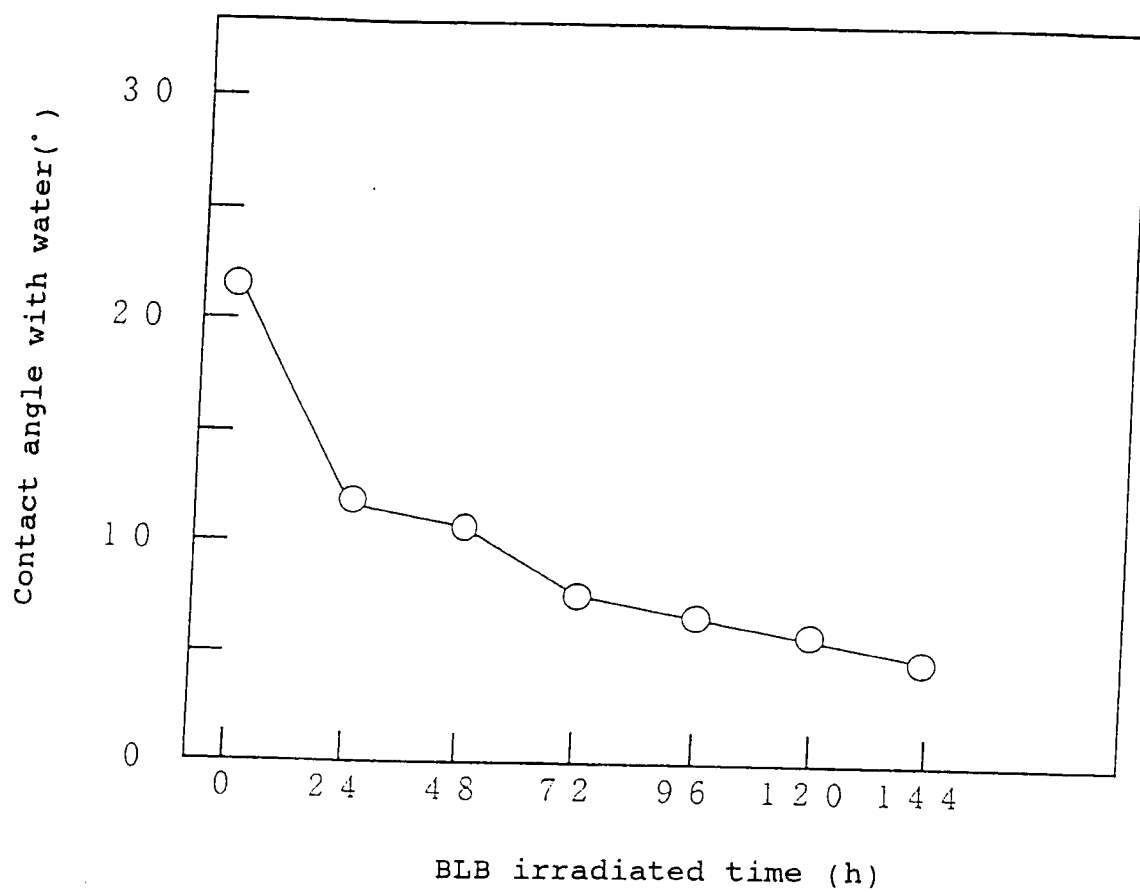


Fig. 45

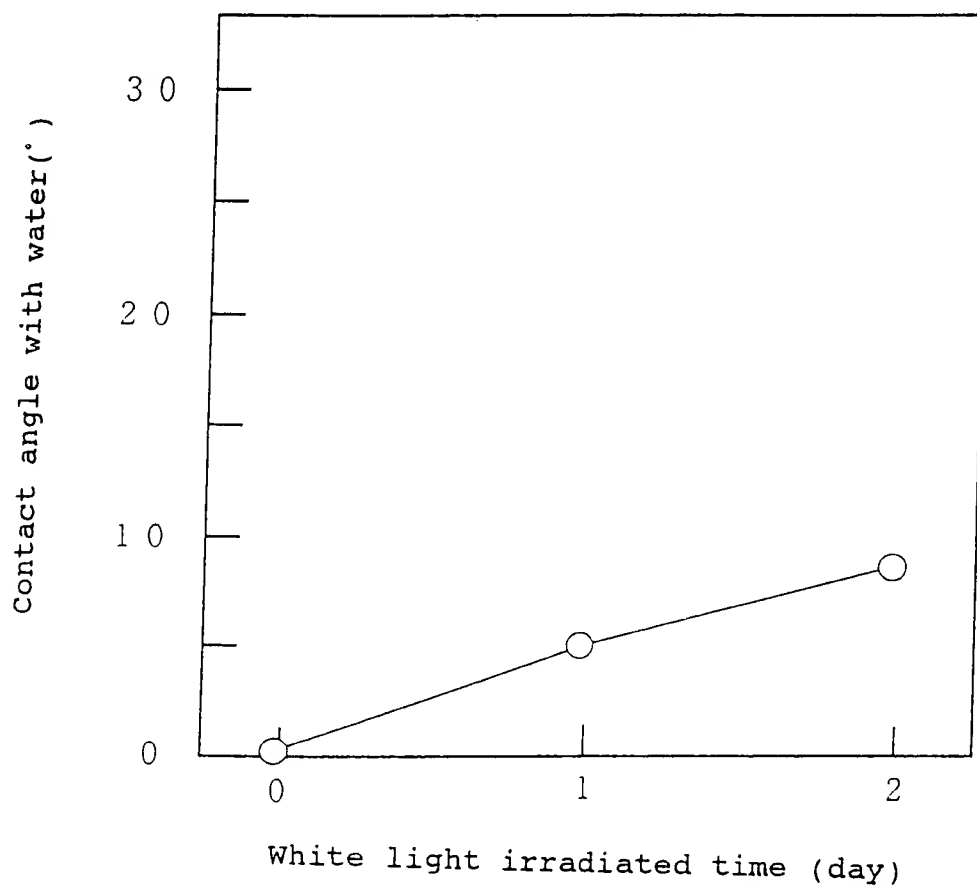


Fig. 46

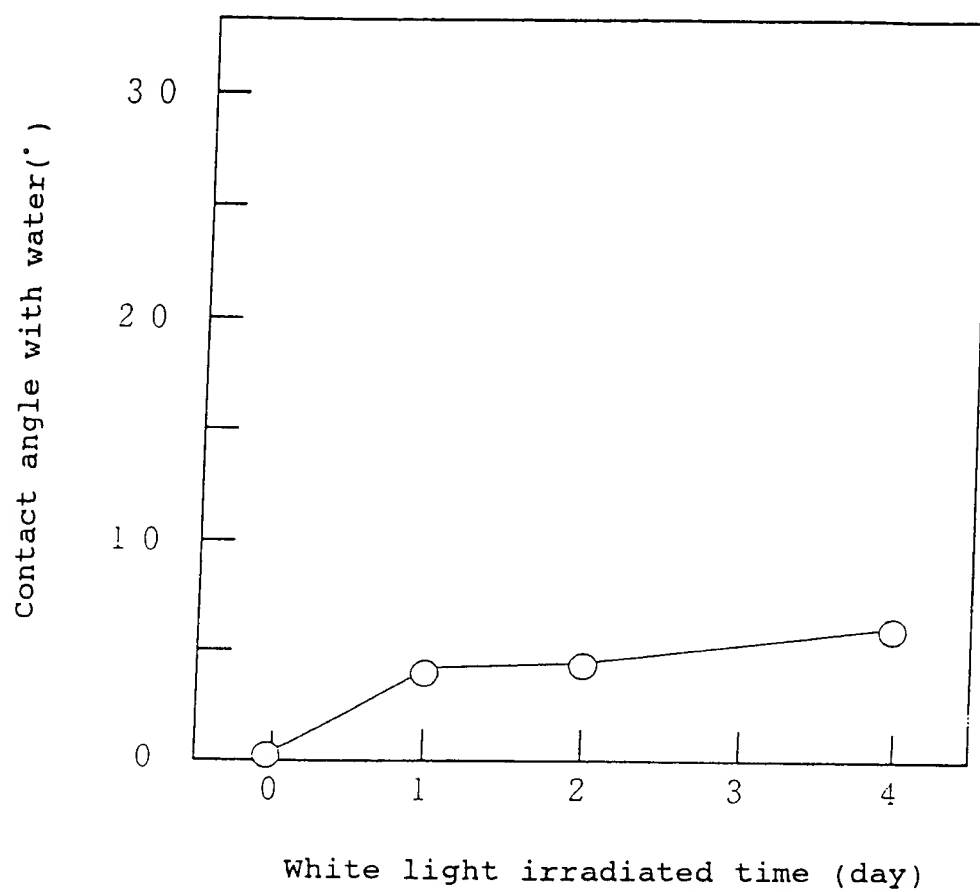


Fig. 47

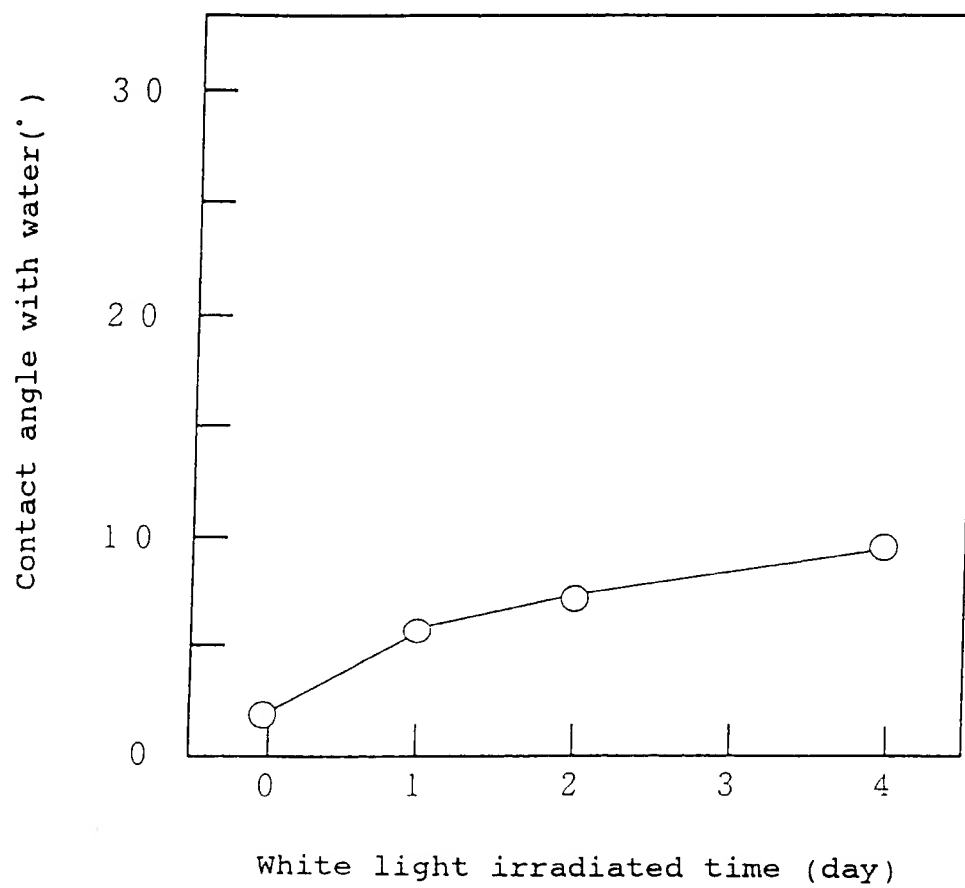


Fig. 48

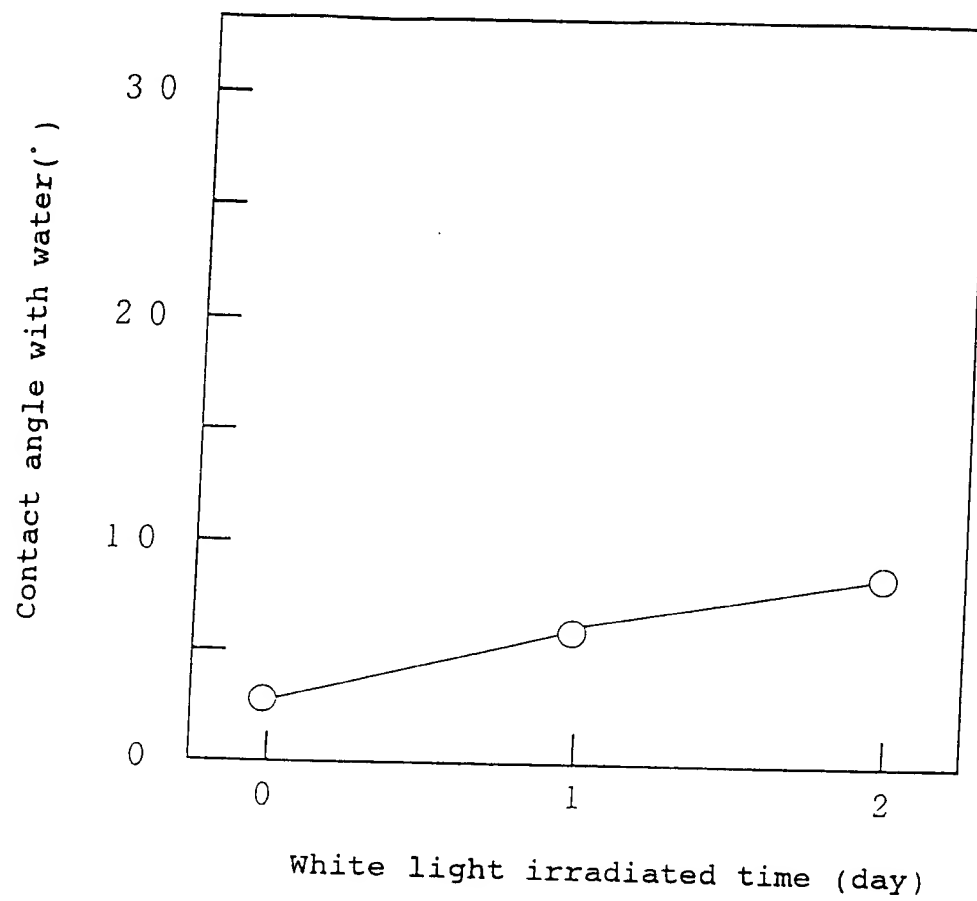


Fig. 49

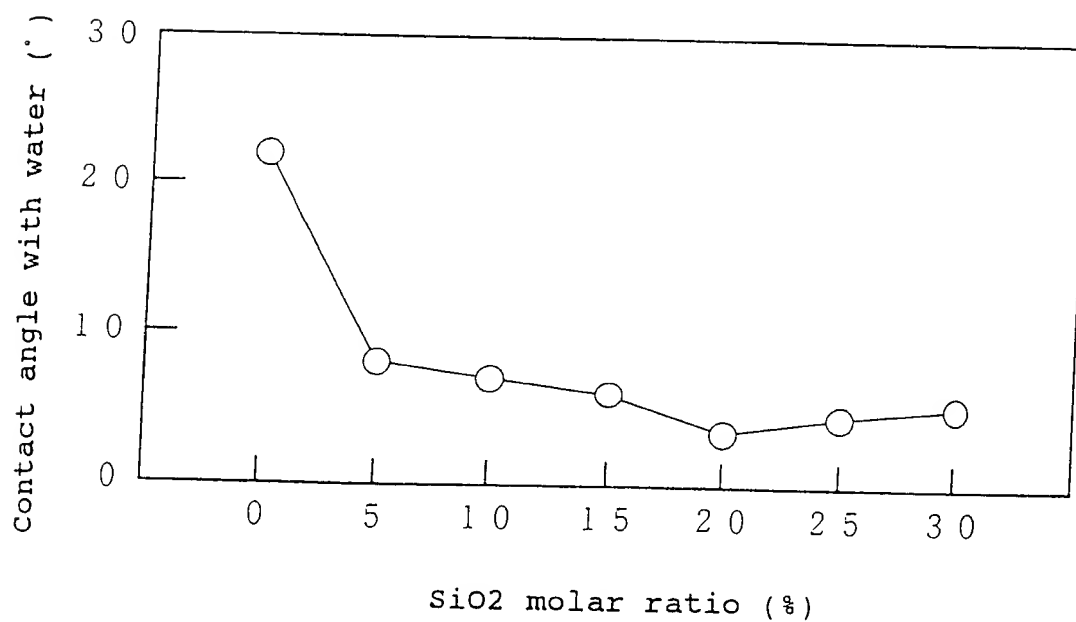


Fig. 50

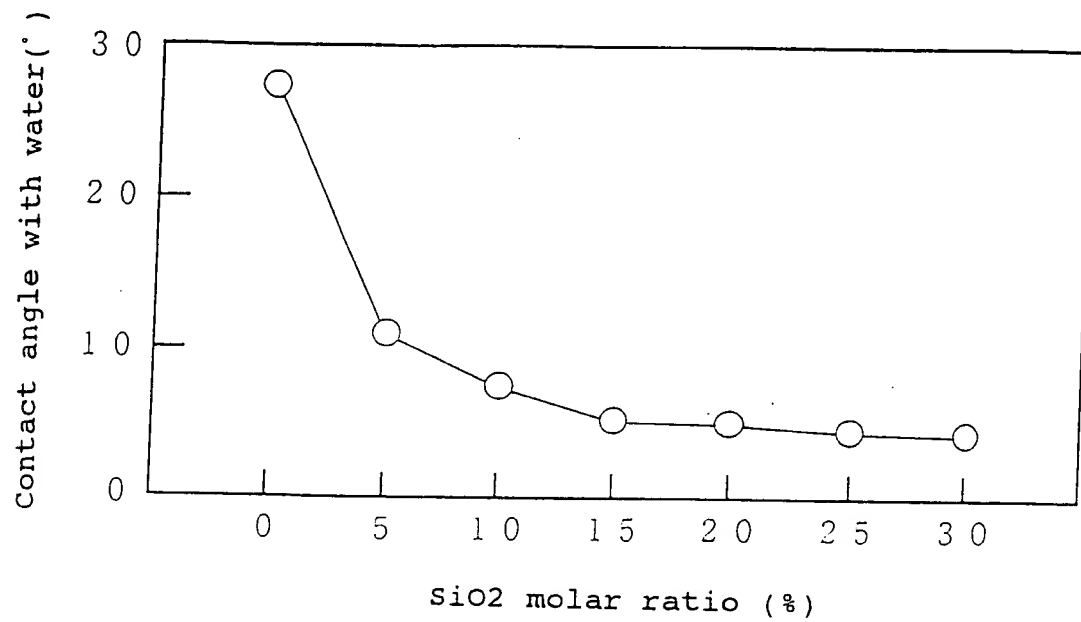


Fig. 51

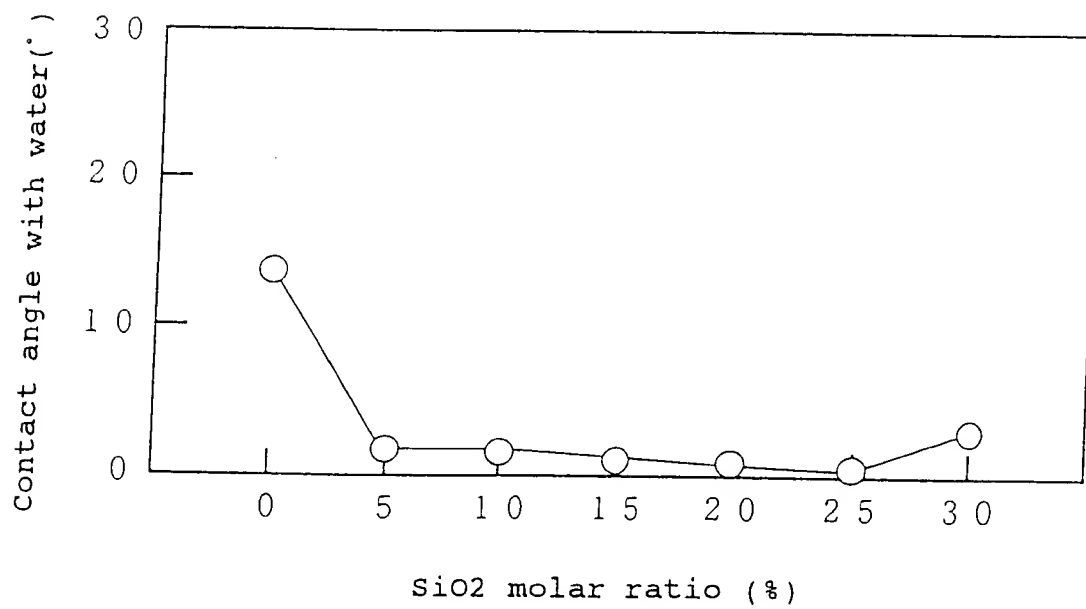


Fig. 52

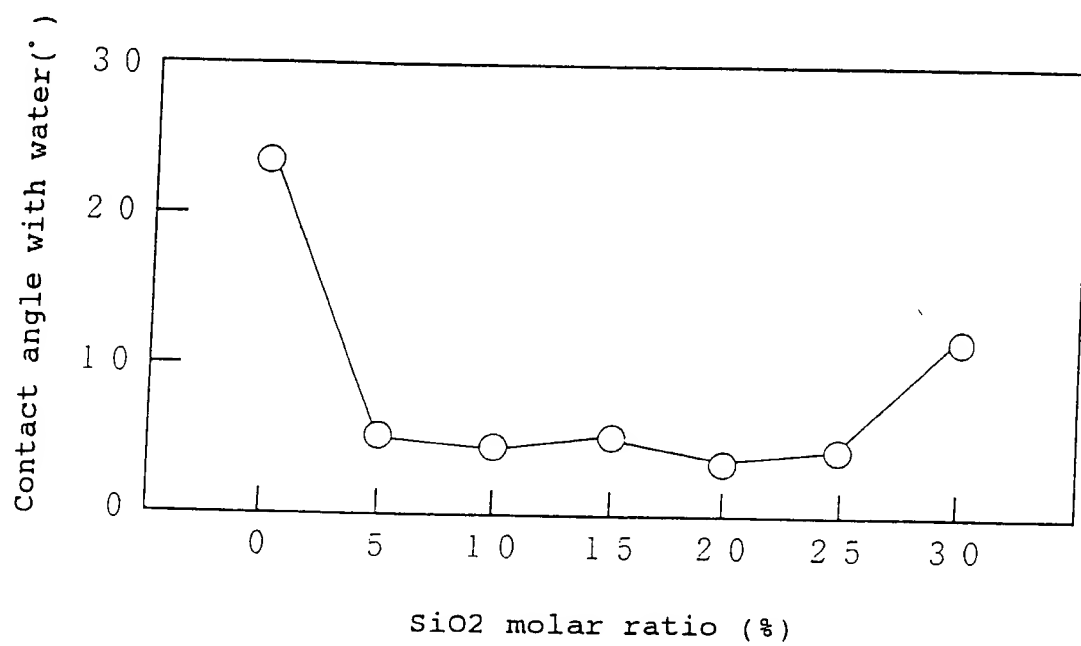


Fig. 53



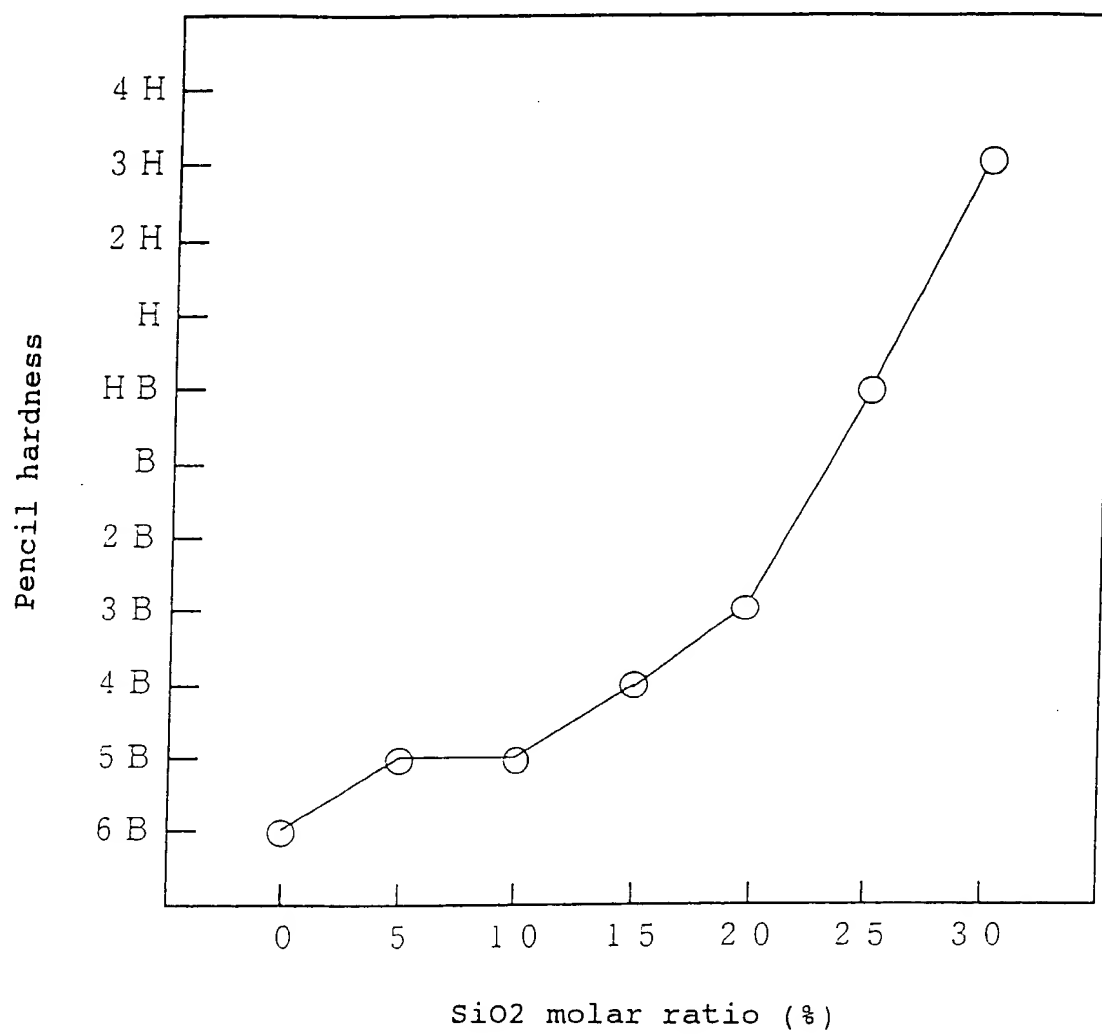


Fig. 54

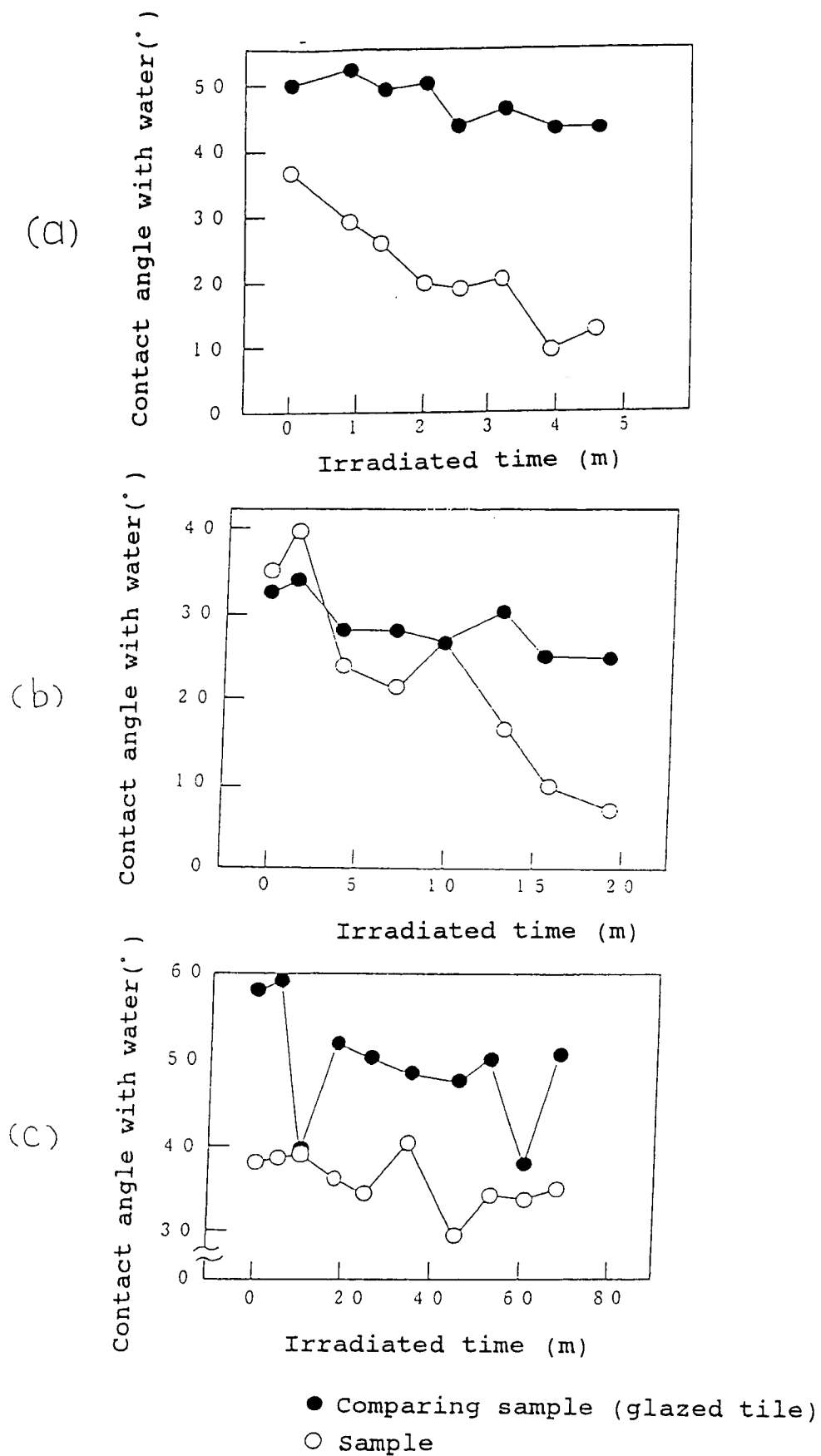


Fig. 55

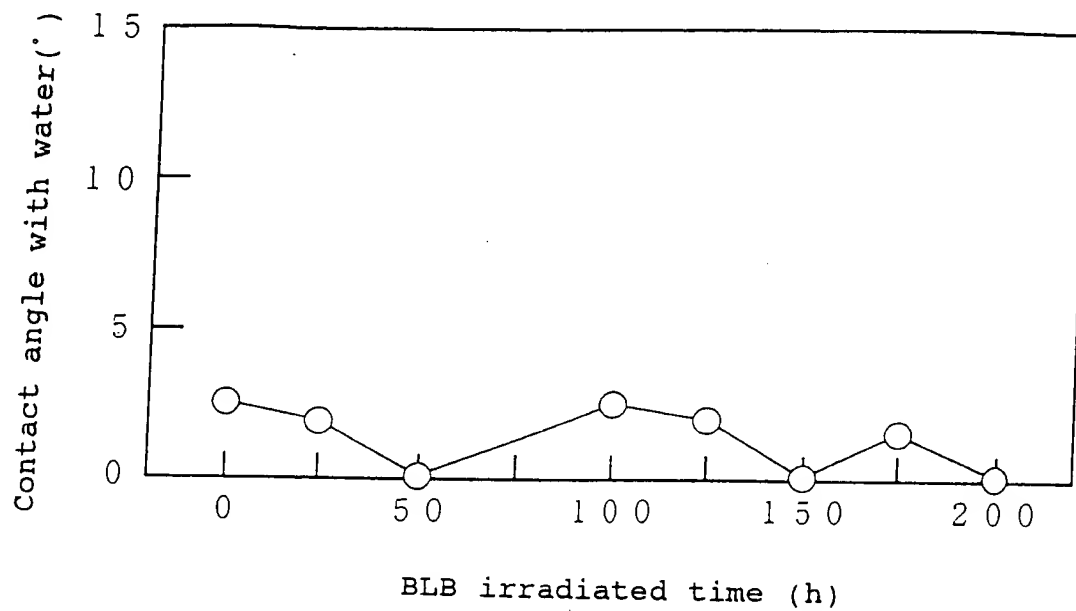


Fig. 56

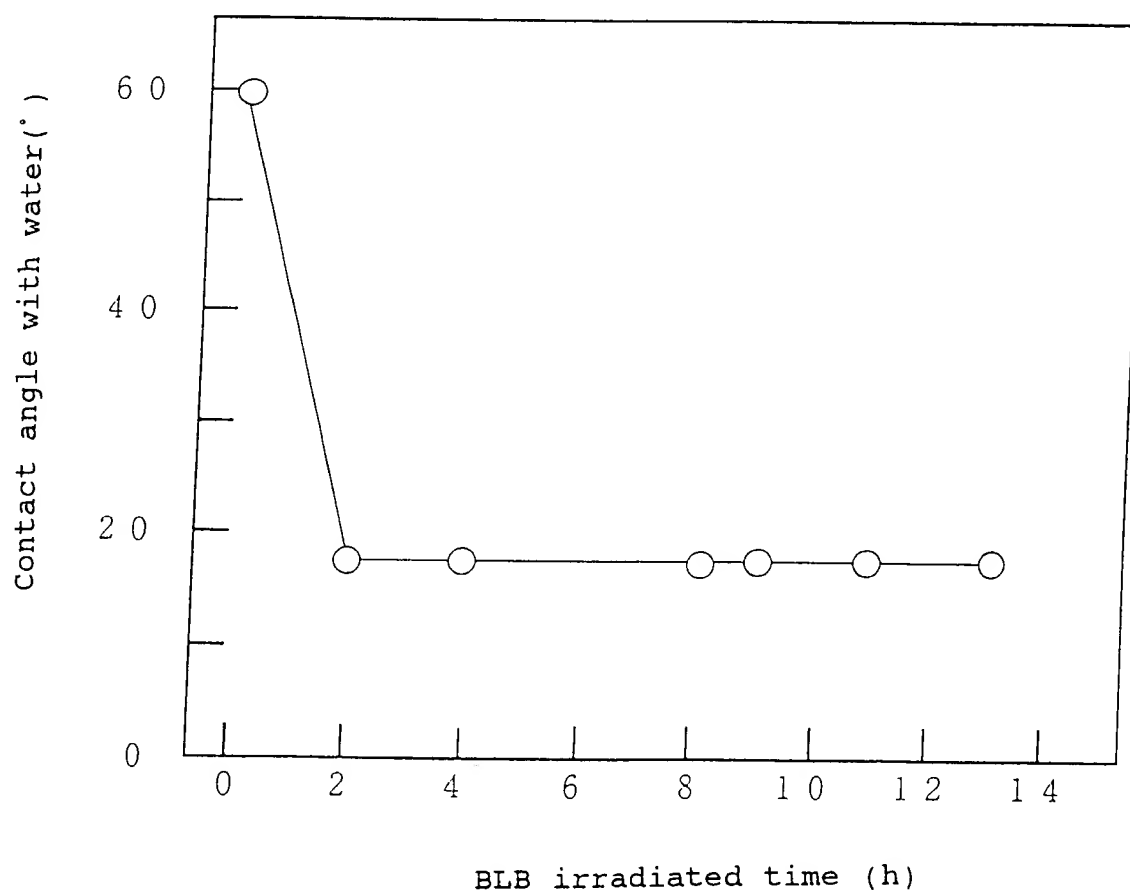


Fig. 57

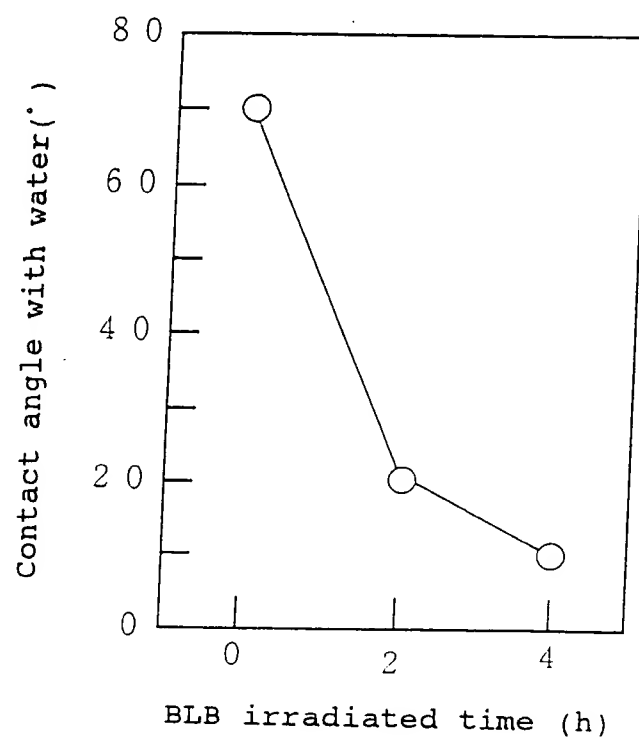


Fig. 58

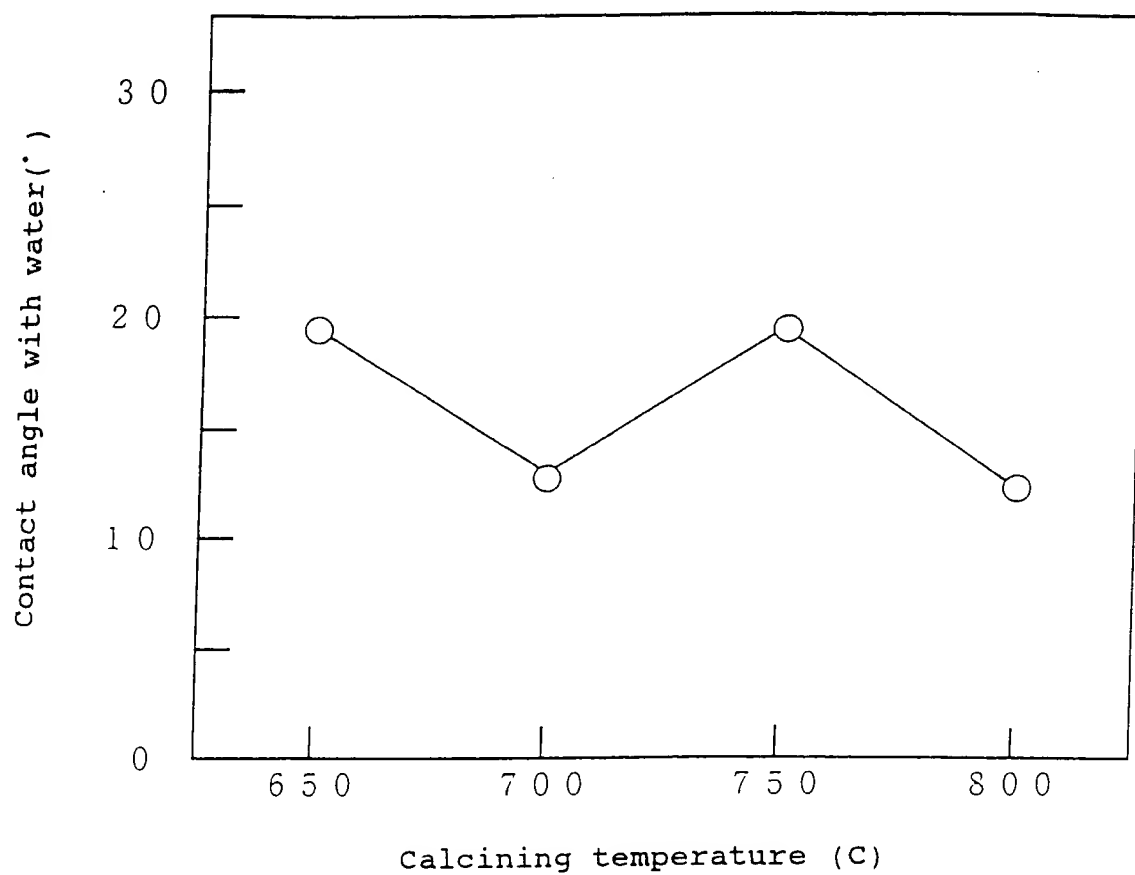


Fig. 59

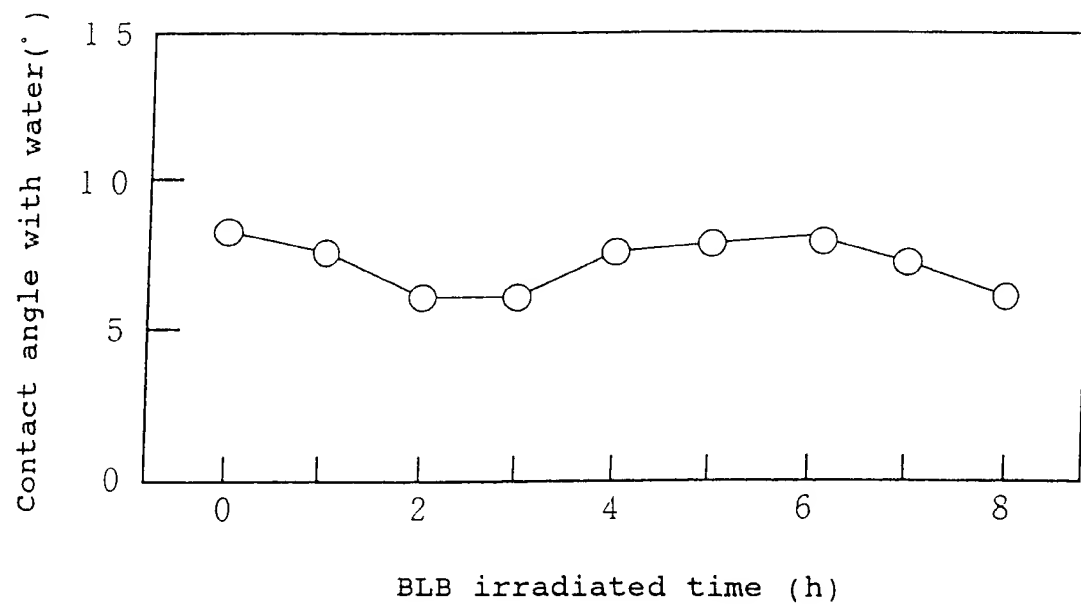


Fig. 60

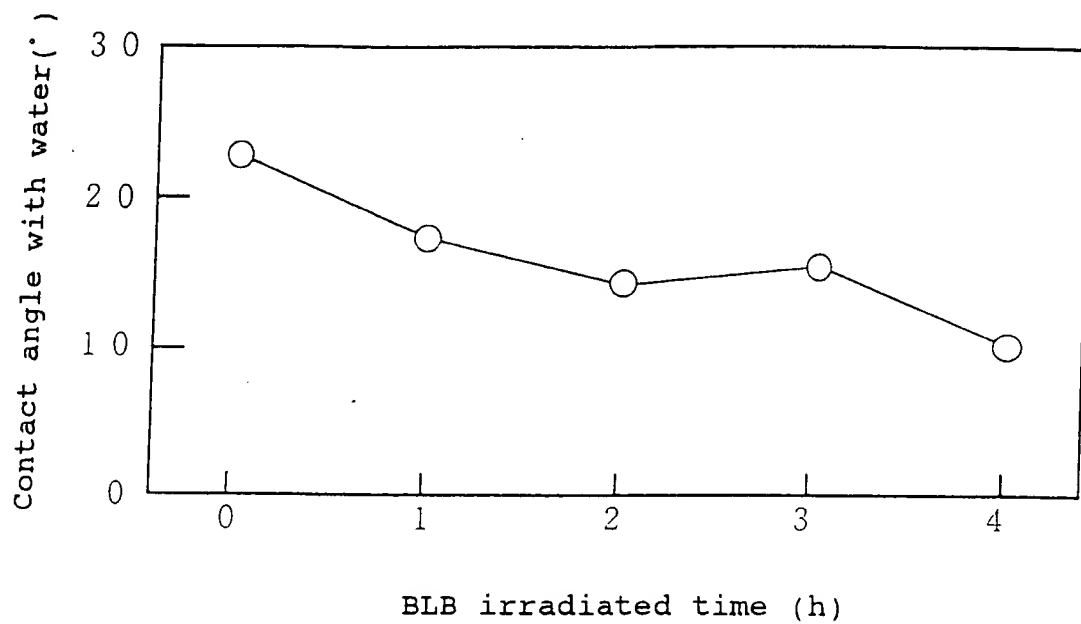


Fig. 61

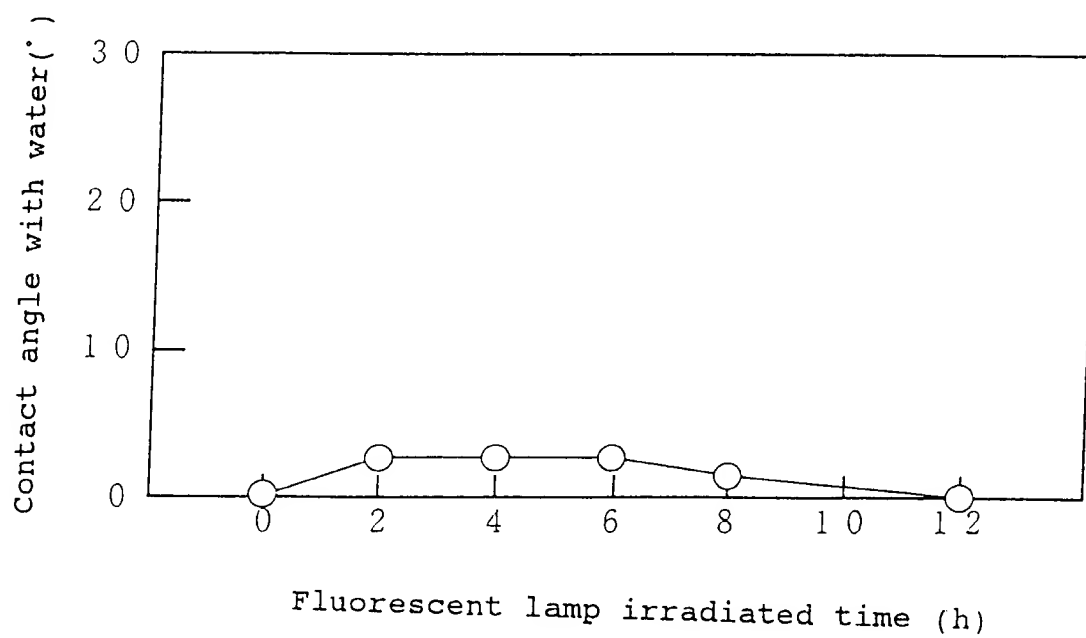


Fig. 62

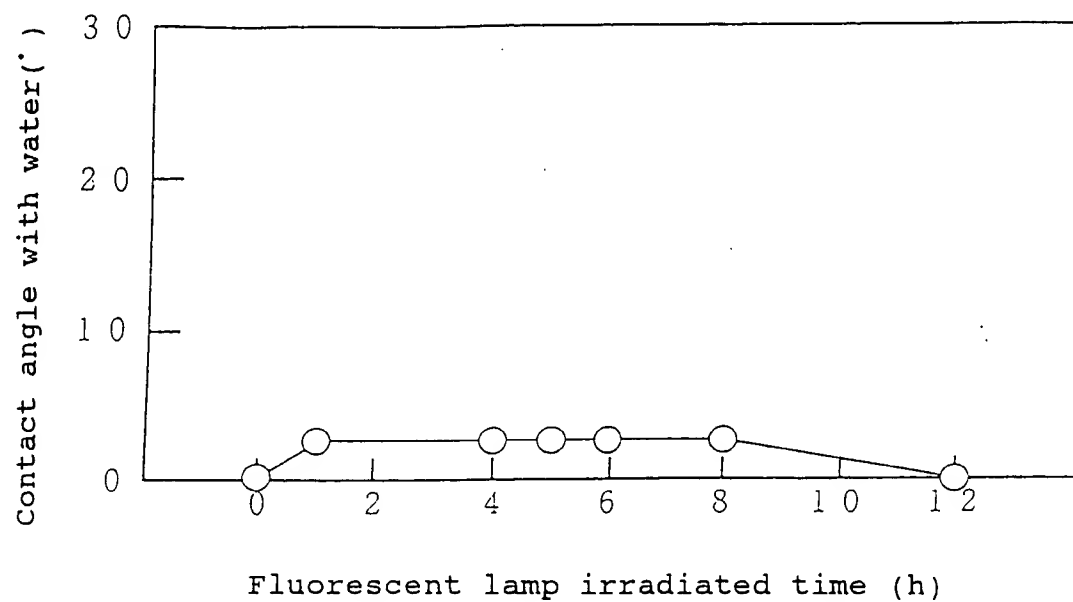


Fig. 63

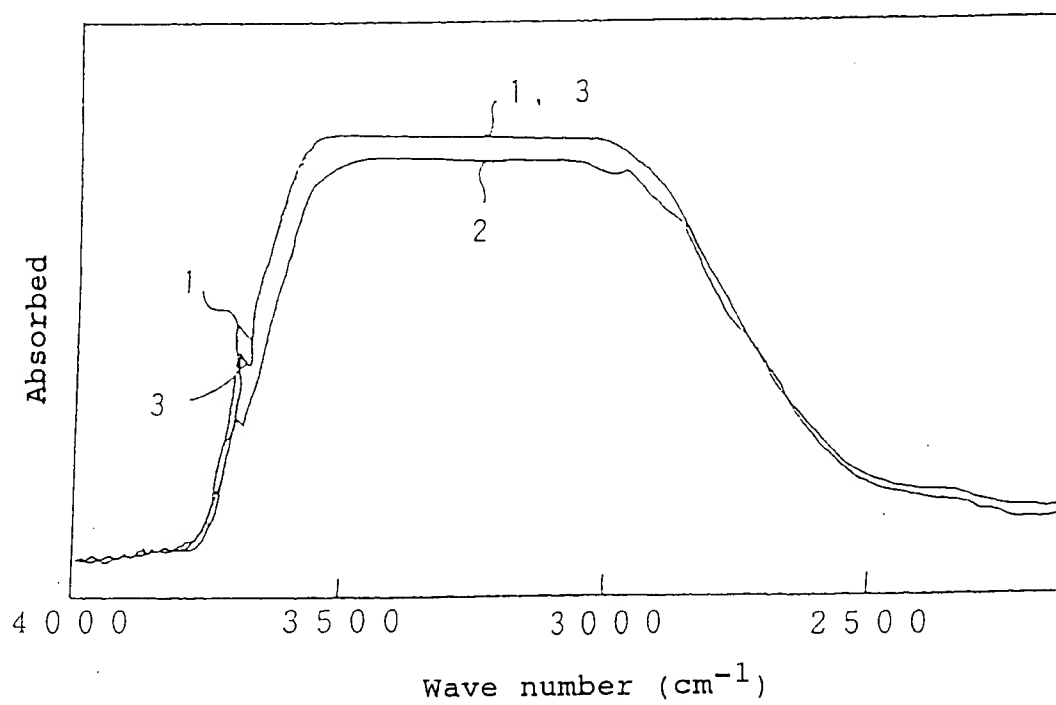


Fig. 64

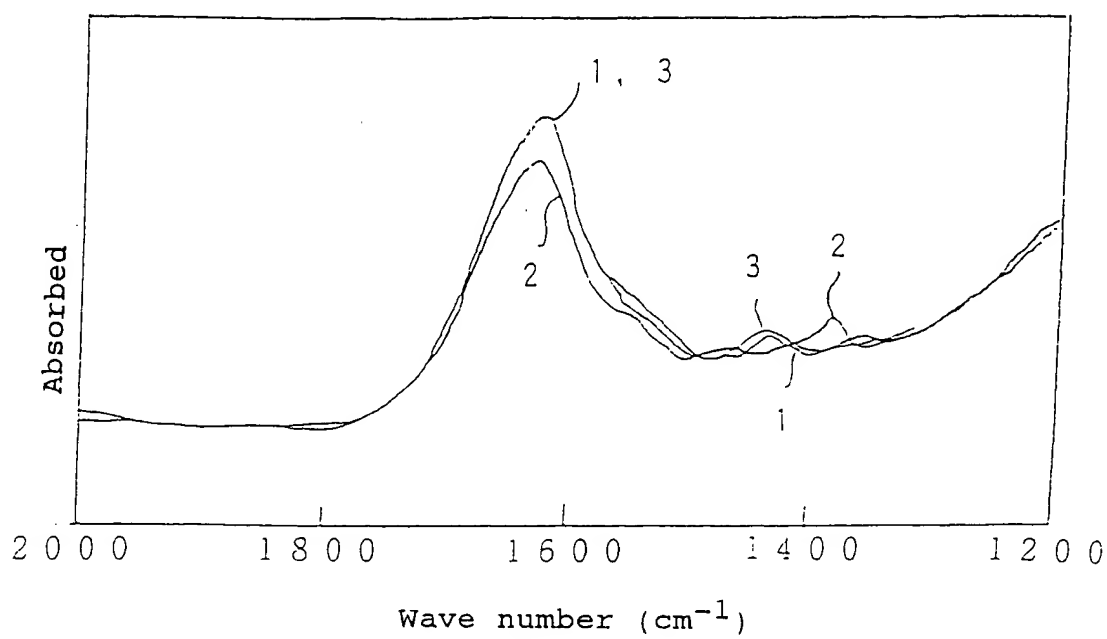


Fig. 65

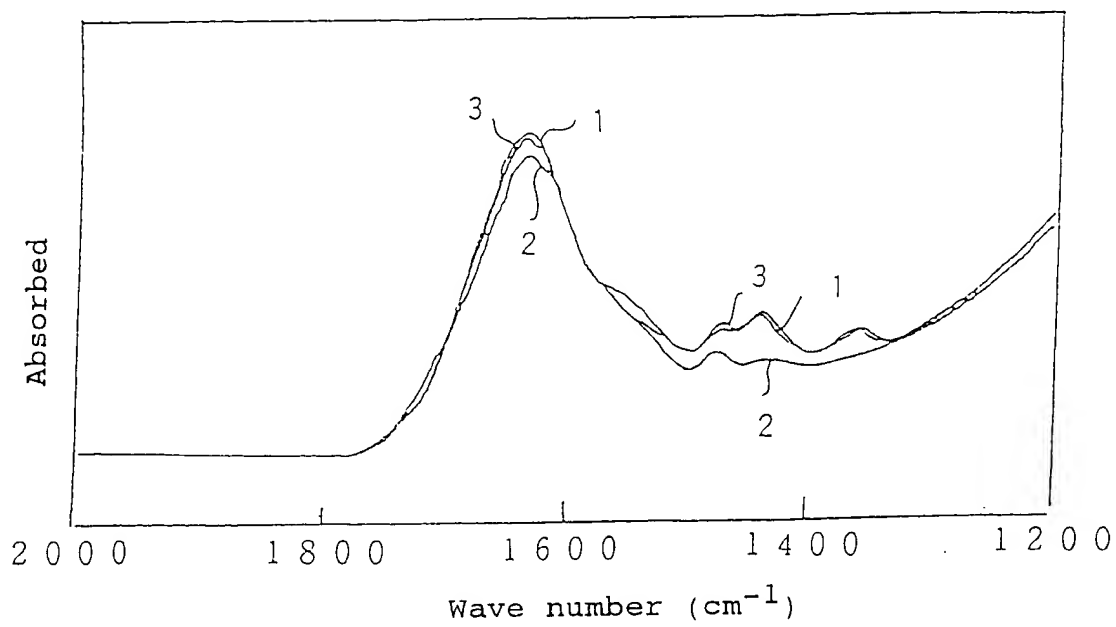


Fig. 66



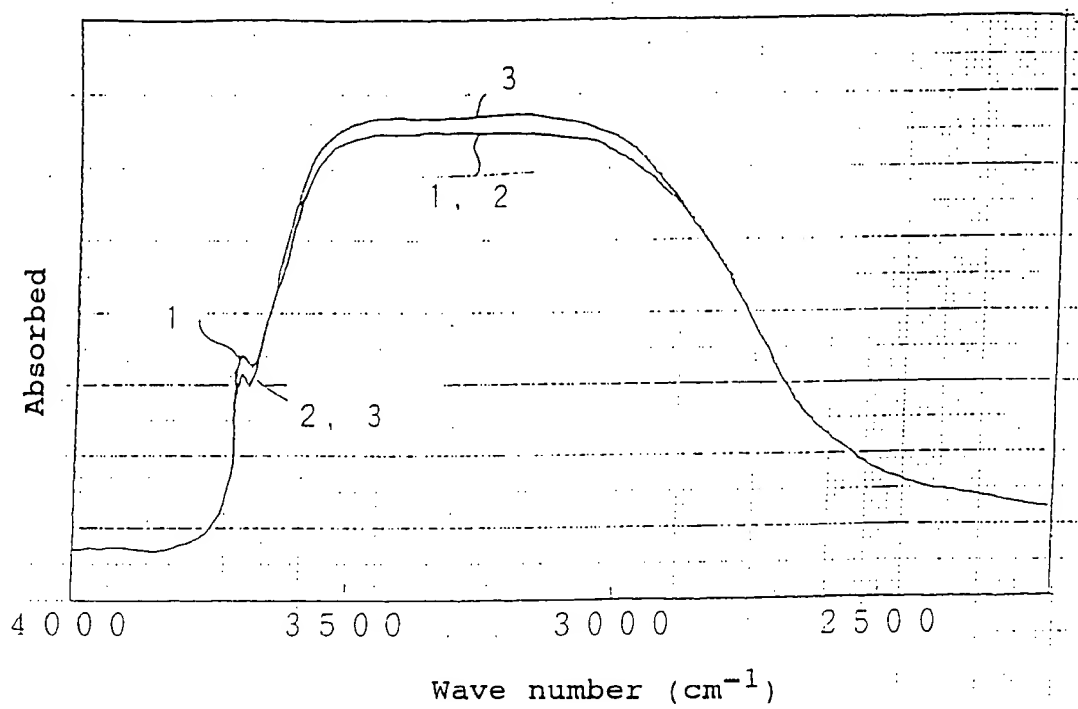


Fig. 67

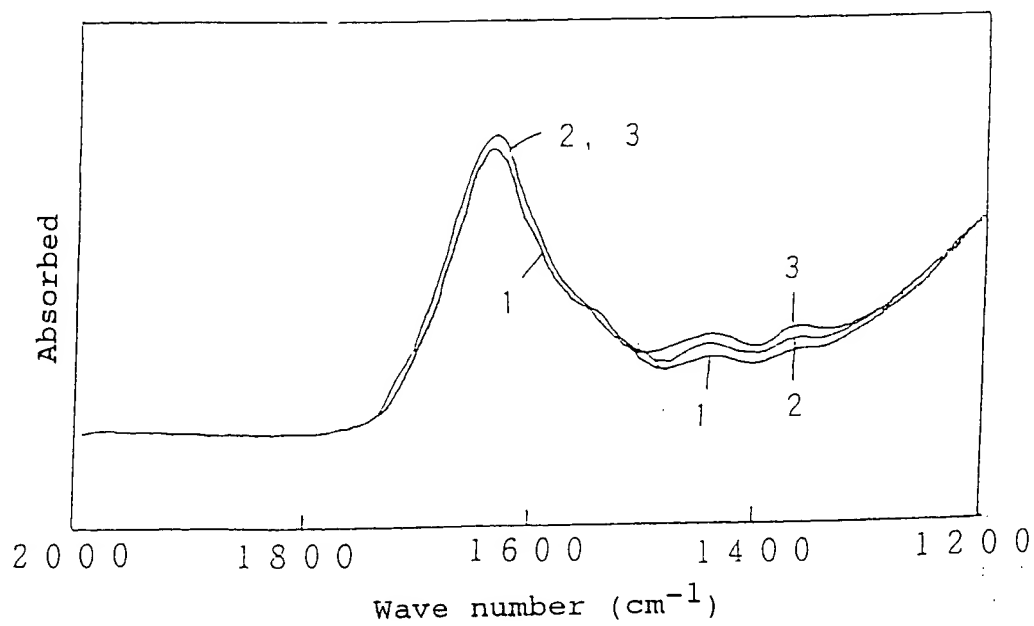


Fig. 68

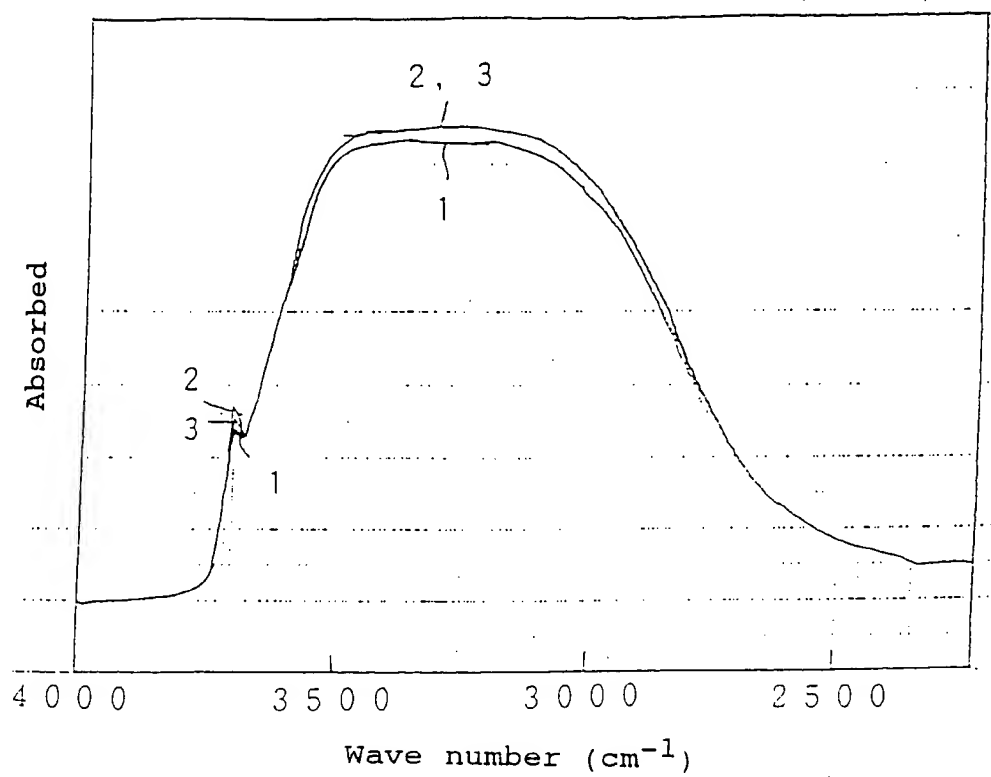


Fig. 69

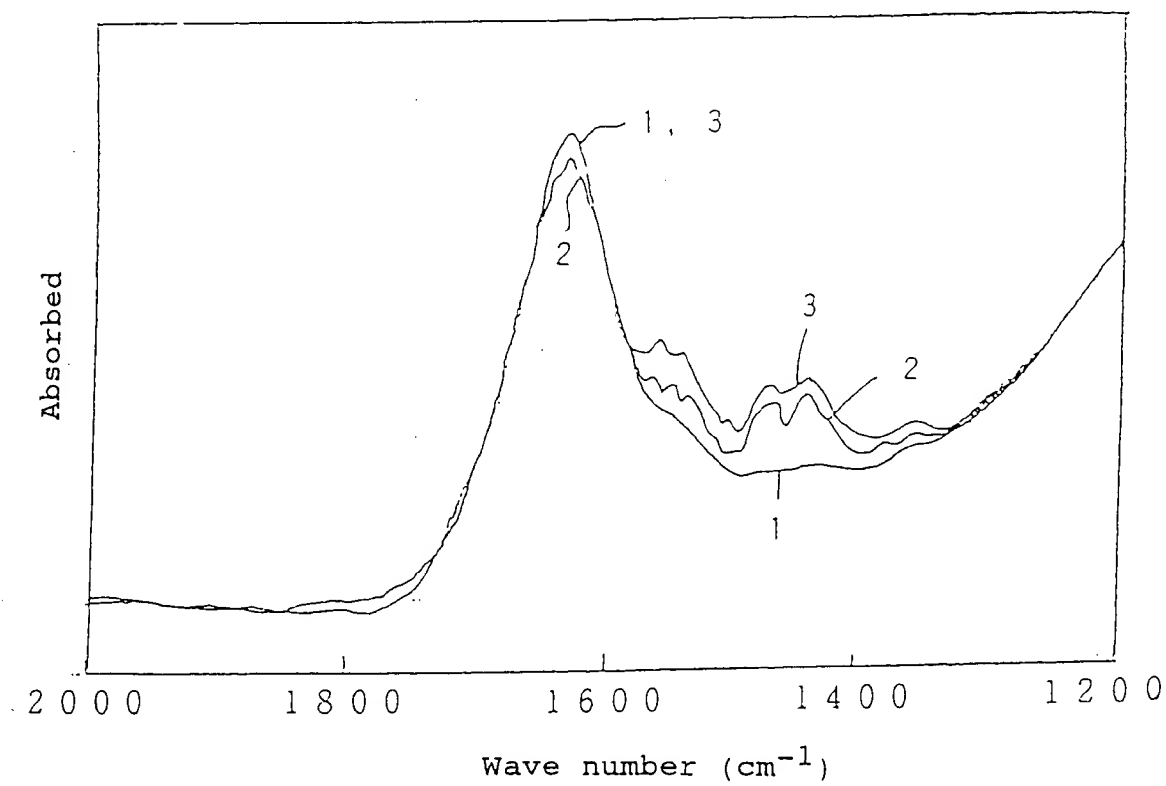


Fig. 70

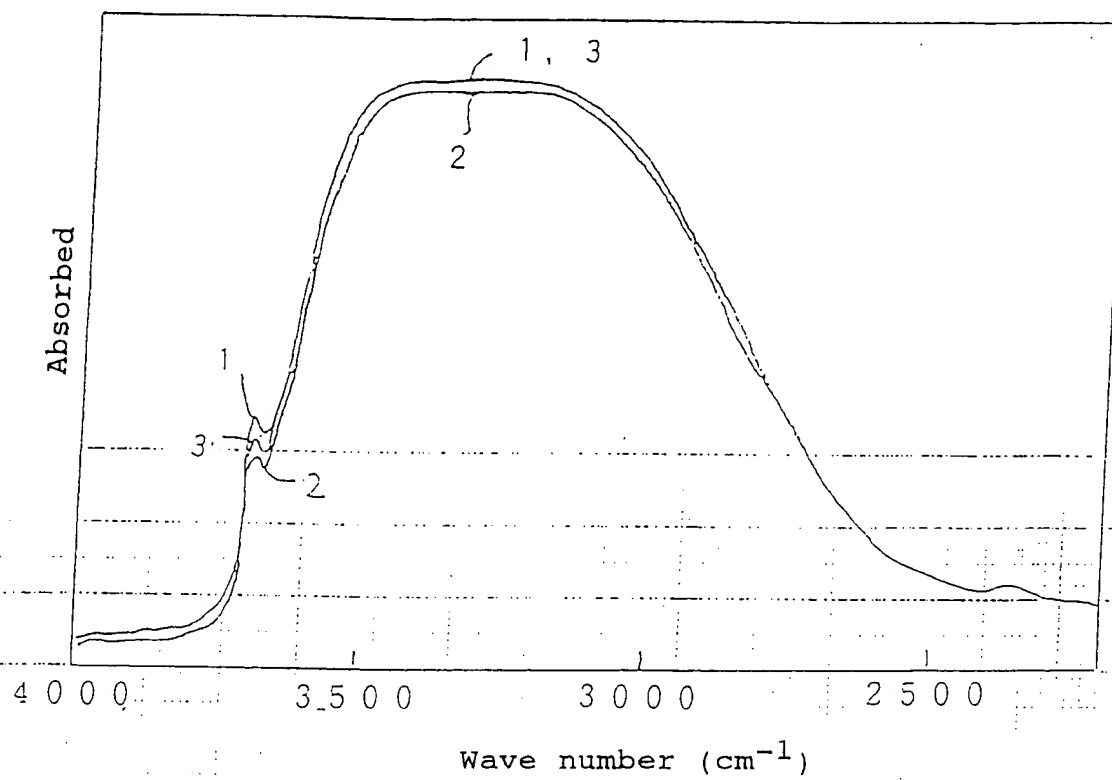
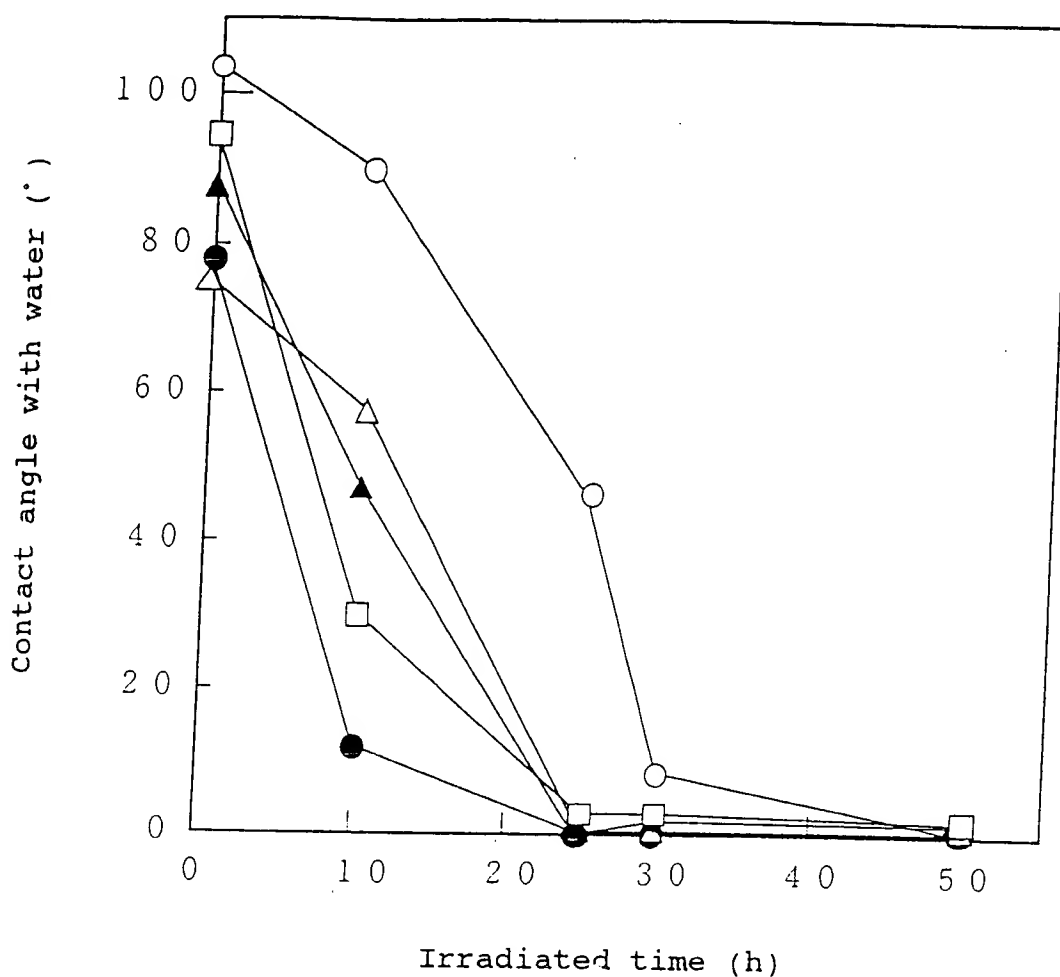


Fig. 71



- Film thickness of a mixed layer 2.5  $\mu\text{m}$
- △ Film thickness of a mixed layer 0.6  $\mu\text{m}$
- Film thickness of a mixed layer 0.2  $\mu\text{m}$
- ▲ Film thickness of a mixed layer 0.1  $\mu\text{m}$
- Film thickness of a mixed layer 0.03  $\mu\text{m}$

Fig. 72

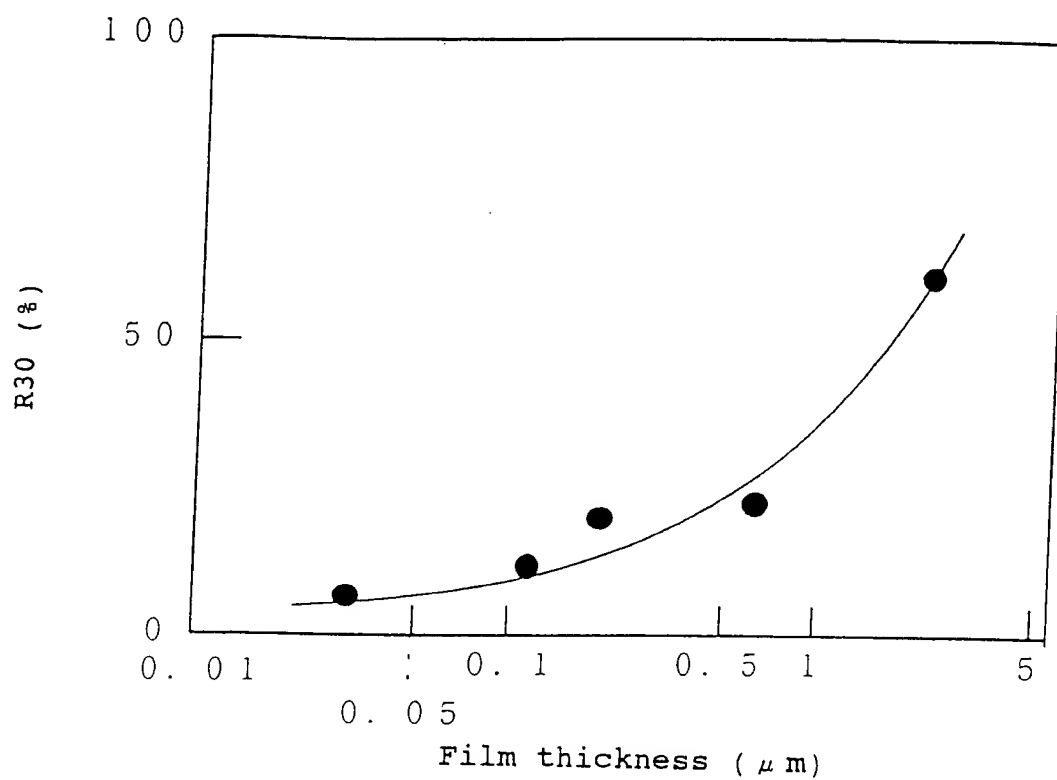


Fig. 73

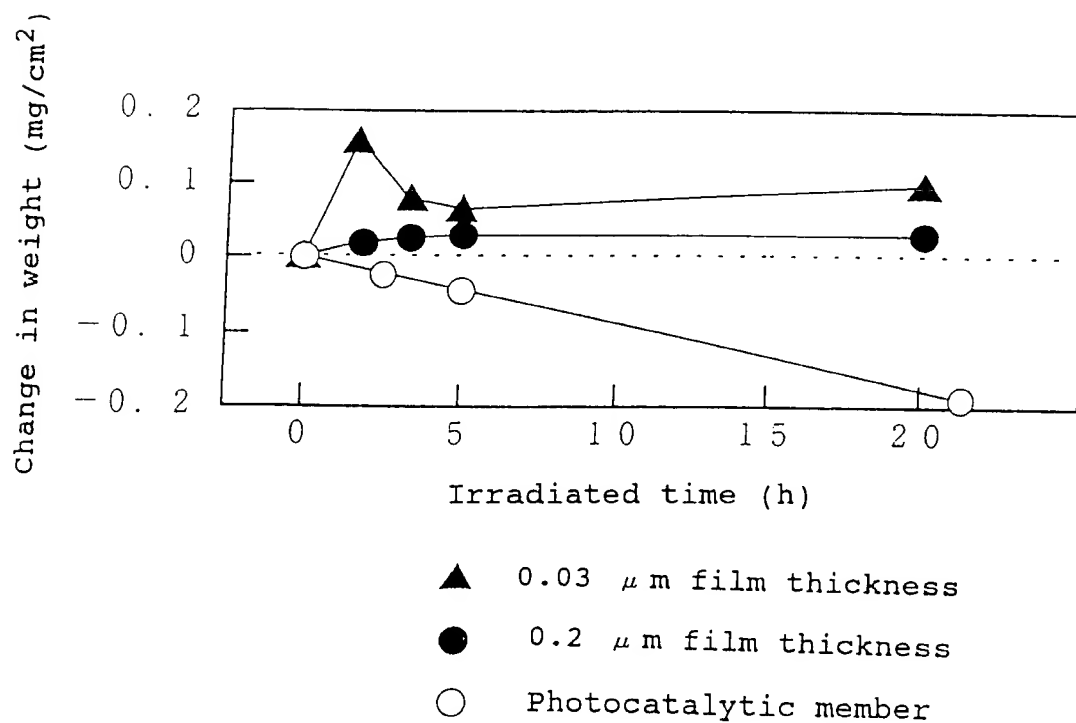


Fig. 74

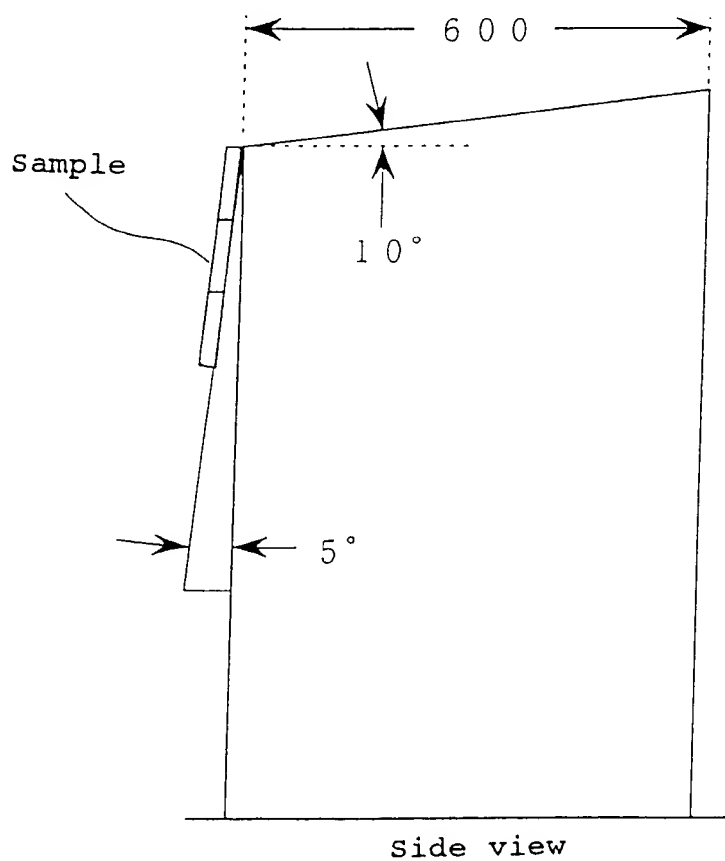
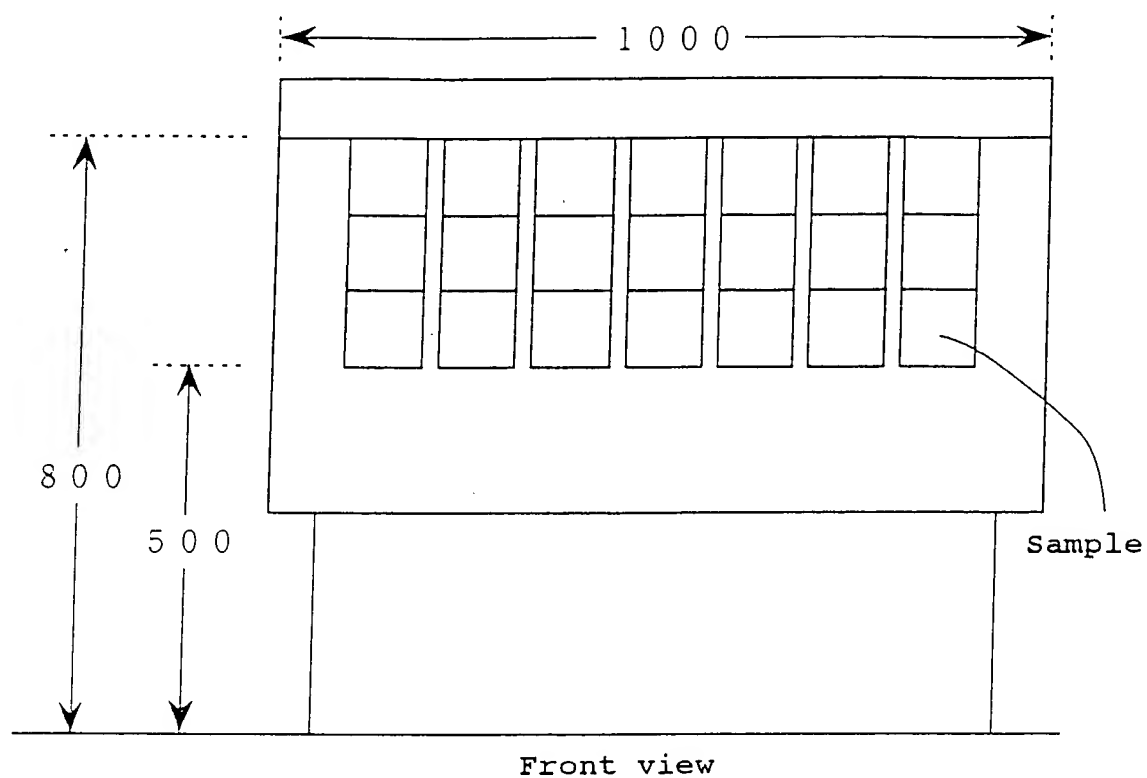


Fig. 75

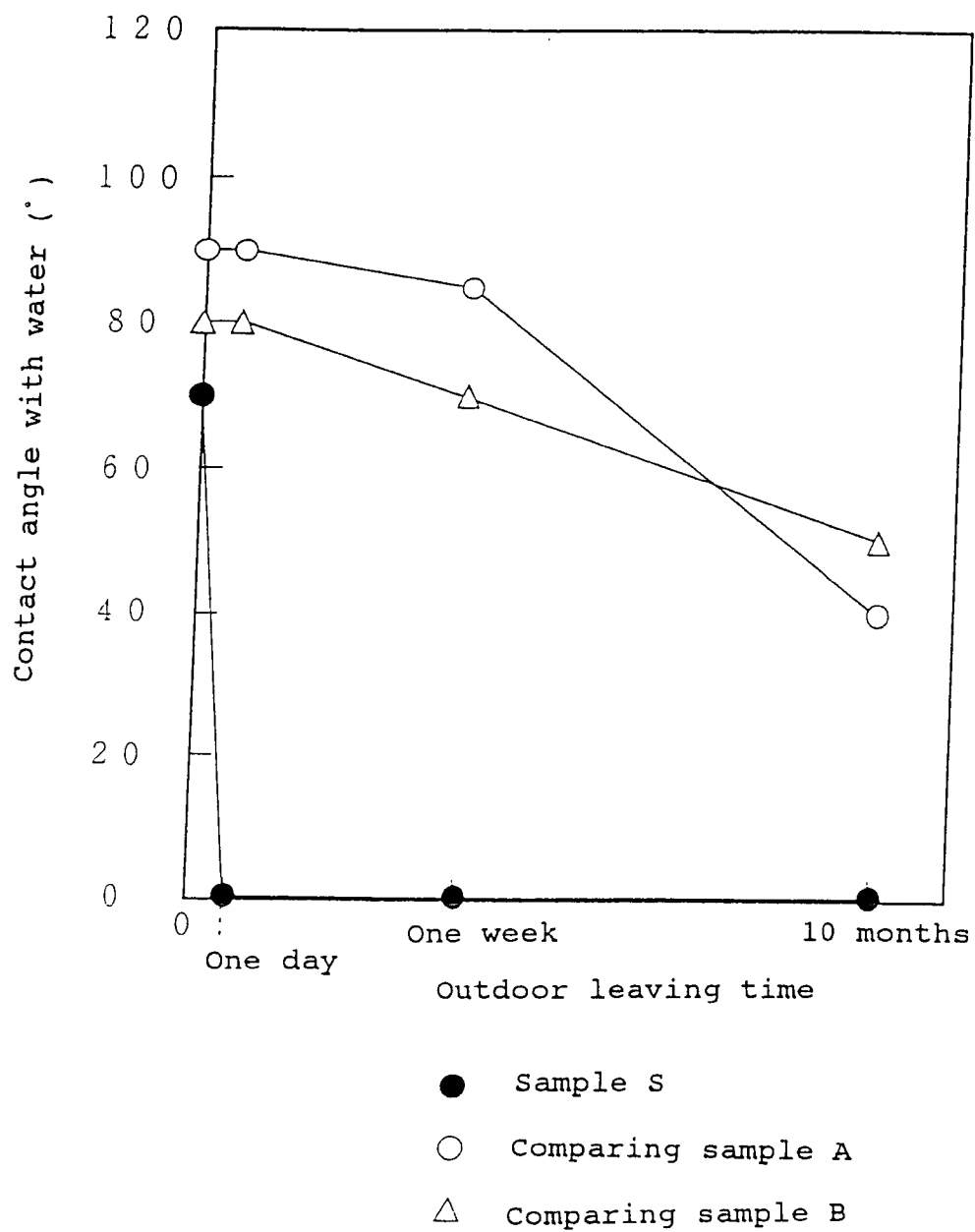


Fig. 76

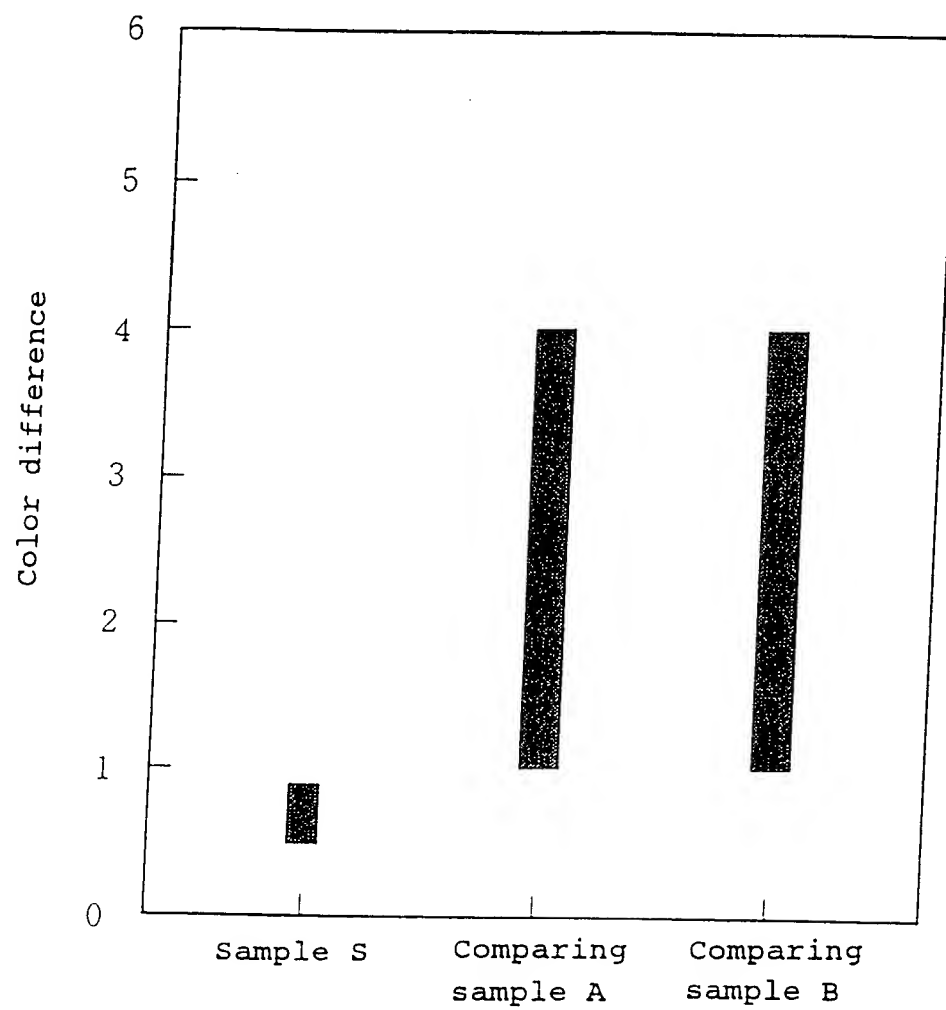


Fig. 77



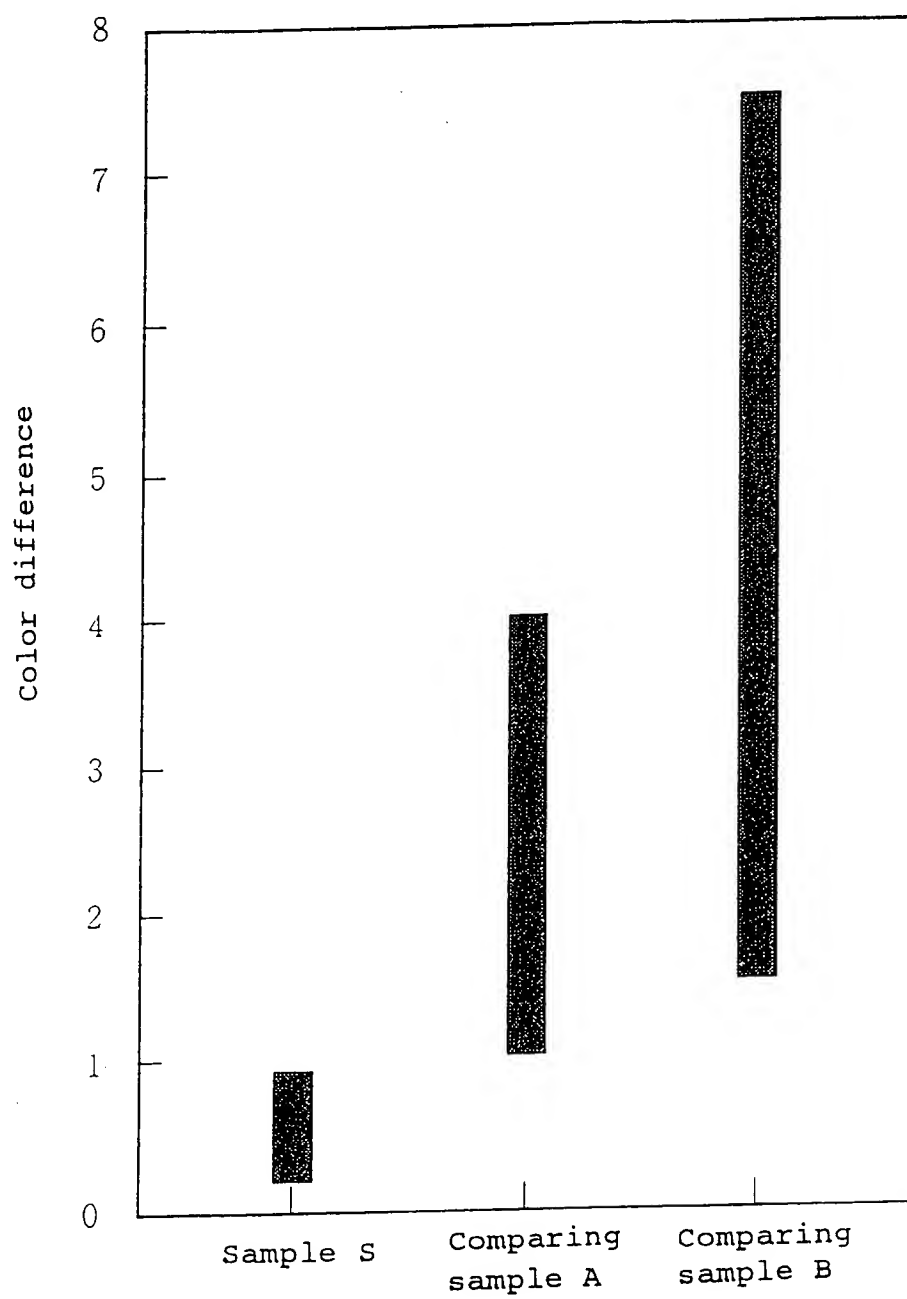


Fig. 78

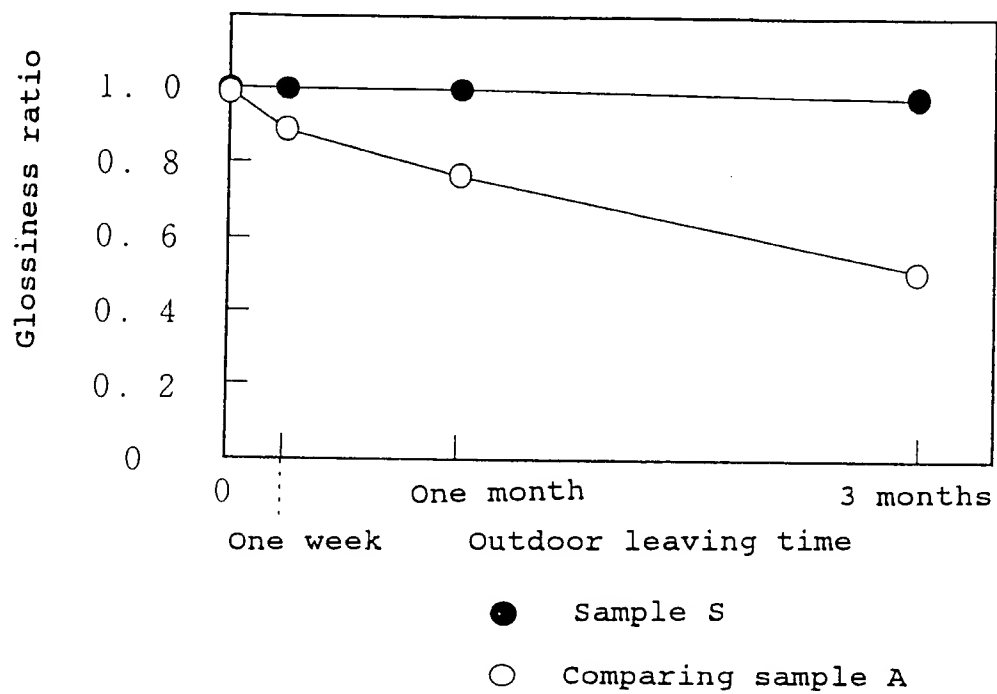


Fig. 79

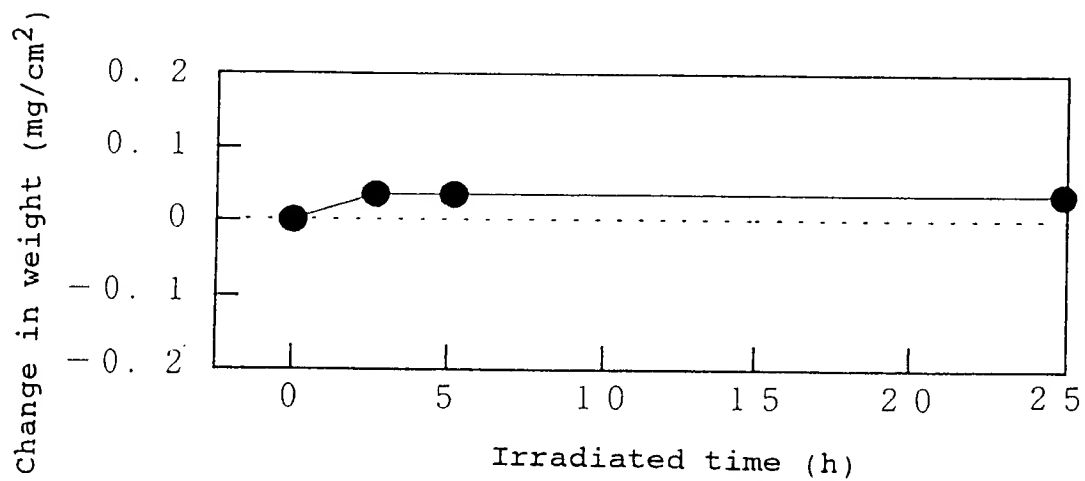


Fig. 80

## Abstract

### [Object]

To provide a translucent member having a long period of antifogging effect.

### [Constituent]

An antifogging member comprising a hydrophilic exposed surface (5) and a means (6) to sustain the hydrophilic exposed surface.

### [Selected Drawing]

Fig. 3